ABUNDANCE AND DISTRIBUTION OF ARSENIC IN HAWAIIAN SOILS AND SEDIMENTS

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I certify that I have read this thesis and that, in my opinion, is satisfactory in scope and quality as a thesis for the degree of Bachelor of Science in Global Environmental Science.

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ABSTRACT

Arsenic is an element notoriously known for its toxicity even at low concentrations and has been linked to considerable health problems when groundwater supplies are contaminated. The purpose of this research was to determine total arsenic abundance and distribution in the soils and sediments of O'ahu, Hawai'i. Soils and sediments samples were collected from a variety of environments with varying degrees of human impact. Samples were classified as originating from locations of forested (conservation), agricultural, urban, or mixed land use and then dried, ground, and digested in a strong acid solution. Concentrations of Co, Cu, As, Cd, Pb, and U were measured using quadrupole ICPMS.

Concentrations of As in all soils and sediments were found to range from 0.3 to 59.6 μg/g with a mean concentration of 11.1 μg/g. Soils from areas of mixed land use displayed the widest range and highest median As concentration of 19.6 μg/g while soils from areas of agricultural land use displayed the next highest median As concentration of 13.0 μg/g. Strong correlation between measured concentrations of As, Cd, and U suggest the origin of As enriched in the soils and sediments analyzed to be derived from agricultural activity as proposed by previous research. Concentrations of As measured in this research are generally higher than As concentrations previously measured in streambed sediments from O'ahu, Hawai'i, regardless of land use. However, mean As concentrations from areas of agricultural land use are lower than those previously reported in streambed sediments and likely a result of a different experiment design. The median As concentration in the soils and

sediments collected from forested areas (7.2 μg/g) corresponds well with the mean As concentration reported for uncontaminated US soils of 7 μg/g although it is higher than the reported world mean As concentration of 5 μg/g in soils. A total of 42.9% of all soil samples exceed the CCME EQG for As in soils and 7.1% of all beach sands exceed the CCME EQG marine ISQG for As.

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ADP – Adenosine diphosphate (product of ATP dephosphorylation)

amu – atomic mass unit

CCA – Chromated Copper Arsenate

CCME – Canadian Council of Ministers of the Environment

CI – Confidence Interval

cm – centimeter

CRM – Certified Reference Material

CPS – Counts Per Second detected by the mass spectrometer

EPA – Environmental Protection Agency (US)

EQG – Environmental Quality Guideline

eV – electronvolt

g – gram

ICP – Inductively Coupled Plasma

ICPMS – Inductively Coupled Plasma Mass Spectrometry

ISQG – Interim Sediment Quality Guideline

IUPAC – International Union of Pure and Applied Chemistry

K – Kelvin

km – kilometer

LD_{50} – Lethal dose for half the test population

LOD – Limit of Detection

m – meter

mm – millimeter

Ma – Million years ago

MCL – Maximum Contaminant Level

mg – miligram

m/z – mass-to-charge ratio

ng – nanogram

NRC – National Research Council

PEL – Probable Effect Level

r – Pearson's correlation coefficient

s – second

s – standard deviation

SPM – Suspended Particulate Matter

t – ton

Torr – mmHg

WHO – World Health Organization

%RSD – Percent Relative Standard Deviation

µg/g – microgram per gram (ppmw)

µg/L – microgram per liter (ppbv)

US – United States

°C – degrees Celsius

INTRODUCTION

The presence of arsenic (As) is universal in nature. Arsenic, a metalloid in group 5A of the periodic table, is the 47th most abundant of the 88 naturally occurring elements. It is the twentieth most abundant element in the Earth's crust, with an average concentration of 2-3 μg/g (Wedepohl, 1995). However, natural As concentrations are highly variable and are chiefly determined by the geologic history of the area, as weathering of As containing rocks is considered to be the dominant source of As to the environment (Tamaki and Frankenberger, 1992). Volcanic eruptions and hydrothermal activity are also natural sources of As into the environment (Matschullat, 2000). The metalloid has only one stable isotope (^{75}As), forms a large assortment of both organic and inorganic compounds, and strongly complexes to solid metal oxides when present as an oxyanion. The most important minerals containing As are metal sulfides. Mining of sulfide ores provides important metal resources in many areas but mining activities often concentrate As and release it to the environment in large quantities (e.g. Matschullat, 1996; Matschullat et al., 2000).

Arsenic compounds are perhaps most commonly known for their toxic properties. Reference to a toxic substance now suspected to be As was made by Greek philosopher Aristotle in the 4th century BC and As compounds were used in the poisoning murders characteristic of imperial Rome (Vaughan, 2006). Furthermore, experts now believe that French emperor Napoleon Bonaparte was poisoned with arsenic while imprisoned after his defeat in the Battle of Waterloo (Vaughan, 2006). There have been several occurrences of mass As poisonings within the last century. In

1900, consumption of arsenic contaminated beer resulted in the poisoning of 6,000 people in the Manchester district of England; 80 of these victims died (Reynolds, 1901). In 1955, over 12,000 Japanese infants were poisoned with As contaminated dried milk; 130 infants died (Yamashita et al., 1972). Another 400 people were poisoned in Japan in 1956 by soy sauce contaminated with As (Mizuta et al., 1956). In 1972, eleven cases of poisoning occurred in western Minnesota, where well water and soil levels were found to be elevated due to contamination from grasshopper bait placed on the ground in the 1930s (Feinglass, 1973). In 1987, a total of 307 cases of acute As poisoning were reported in Buenos Aires, Argentina, where vandals broke into a butcher's shop and poured sodium arsenite over the meat (Roses et al., 1991).

The well-documented toxic properties of various As compounds have provided motivation for many of their applications. Arsenic compounds have been used as pesticides, wood preservatives, drying agents, dyes and coloring agents, and pharmaceuticals as well as being used in ore production and processing, metal treatment (including galvanization), ammunition production, electronics industries, and glass ware production (Matchullat, 2000). Arsenic is also released through high-temperature combustion associated with oil and coal burning, waste incineration and cement production and is present in fertilizers, municipal sewage, and animal waste (Matchullat, 2000). Awareness of the detrimental effects of low concentrations of As in the environment has grown and consumption has been decreasing. For example, the last agricultural application of inorganic As pesticide in the US was canceled in 1993 although organic arsenicals still remain in a few pesticides (Abernathy et al., 2003). Furthermore, US wood treatment and manufacturing industries voluntarily

agreed to stop using chromated copper arsenate (CCA) wood preservatives by the end of 2003.

Arsenic contamination of groundwater is causing massive health problems in various areas of the world. Millions of people in West Bengal and Bangladesh are chronically exposed to low concentrations of dissolved As in what the World Health Organization (WHO) has described as the worst mass poisoning of a human population in history (Smith et al., 2000). Widespread As poisoning has also been reported in Argentina, Chile, Mexico, China, Thailand, and Taiwan. Areas of the world known to have high concentrations of As in aquifers or in surface soils as a result of mining practices or geothermal activity are identified in Fig. 1.

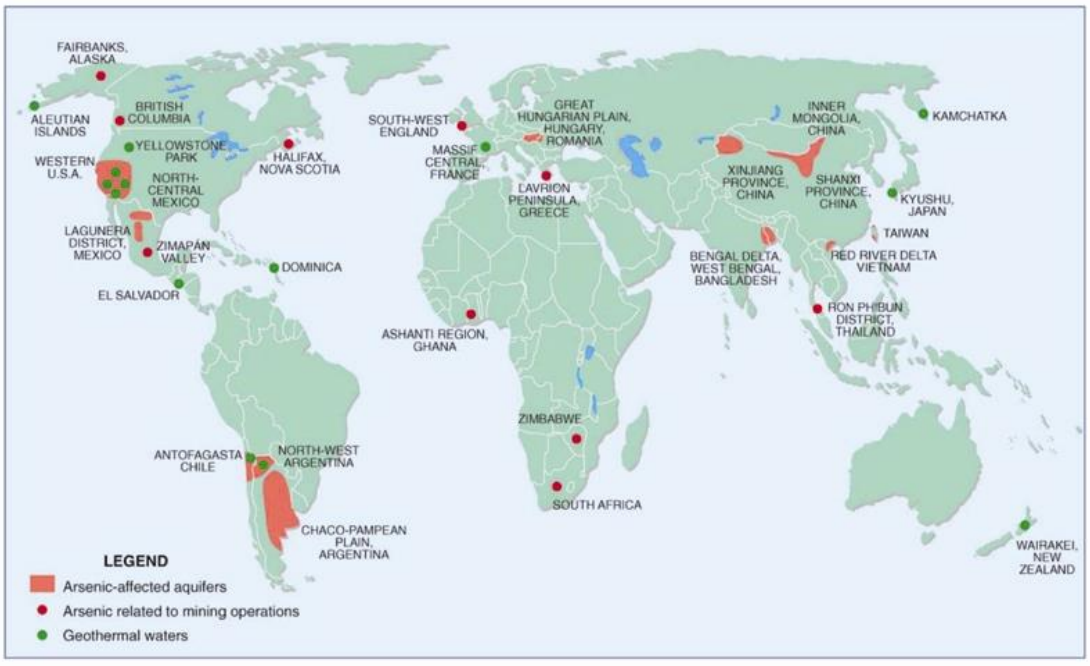

Figure 1. World map showing areas of known elevated As concentrations associated with hydrothermal activity, mining operations or contaminated aquifers. From Smedley and Kinniburgh (2002).

Although levels of As have been determined in many locations, sparse data exist for subtropical volcanic settings. Recently, various studies have been conducted in Hawai'i to determine trace element concentrations in sediments. These examined cores from the Ala Wai Canal, an artificial estuary in urban Honolulu (e.g. De Carlo and Spencer, 1995; Spencer et al., 1995), suspended particulate matter (SPM) in streams from various watersheds on O'ahu (e.g. De Carlo and Spencer, 2002; De Carlo et al., 2004; De Carlo et al., 2005), and soils from agricultural areas on Mau'i (De Carlo and Dollar, 1997). However, few environmental studies focusing specifically on As have been done in Hawai'i. Sediments from Waiakea Mill Pond, the Wailoa River and Hilo Bay were analyzed to evaluate As contamination resulting from the use of As_2O_3 in a cane board manufacturing plant (Hallacher et al., 1985). Yet the lack of available data over widespread areas of the state has created disagreement about the magnitude of natural background levels in Hawai'i and subsequent difficulty in defining areas of elevated As concentrations. The main objective of this research was to perform a survey of total As abundance and distribution in the soils and sediments from a variety of environmental settings on O'ahu, Hawai'i.

1. BACKGROUND

1.1. Geochemistry of Arsenic in Soils and Sediments

Arsenic occurs in the environment in various oxidation states (3-, 0, 3+, and 5+). Arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}) are by far the most common As species in the environment (Stoeppler, 1992). The penta-valent As shows many similarities in chemical behavior with phosphorus due to similar ionic radii and the formation of isostructural oxyanions such as PO_4^{3-} and AsO_4^{3-} (Goldschmidt, 1958). In the soil and sedimentary environments, inorganic and organic arsenic may be present as salts of available cations, in the form of precipitates or as adsorbates on hydrous oxides, clays and other surface active materials (Stoeppler, 1992). Without the intervention of organisms, arsenite and arsenate are expected to be the only arsenic species in the environment (Stoeppler, 1992).

Arsenic is calcophilic and is most often associated with sulfide minerals. However, the more important As minerals are mixed sulfides of the M(II)AsS type where Fe, Ni, Co and other di-valent metals are bonded with arsenic sulfide (e.g. arsenopyrite FeAsS, loellingite $FeAs_2$, realgar AsS, niccolite NiAs, and cobalite CoAsS) (Matschullat, 2000; see Onishi, 1969 for a comprehensive list of the known As minerals). Because As is so often associated with economically lucrative metals, it is often a by-product of mining. Although production has been steadily decreasing, a world total of 37,500 t of AsO_3 was produced in 2004 (Vaughan, 2006).

The lithosphere stores over 10^{13} t As and is by far Earth's largest reservoir (Matschullat, 2000). The pedosphere is estimated to store around 10^9 t As with an average global concentration of 7.5 µg/g As (Goldschmidt, 1958). However, higher

average As concentrations are commonly recorded in soils and sediments. Naturally elevated As concentrations are typically attributed to the weathering environment and As concentration and speciation in the parent rock. Bedrock geology features were found to closely correlate with areas of elevated As in groundwater, stream sediments and rocks in the New England region of the US despite intensive use of arsenical pesticides in the area (Robinson and Ayotte, 2006). Anthropogenically introduced As from mining and smelting activities can also contribute to high As concentrations in soils and sediments. Soils contaminated by historical mining and smelting activities in the Harz mountains of northern Germany were found to have As concentrations ranging from 7-970 μg/g with a median of 130 μg/g (Matschullat, 1996). Even higher As concentrations occur in tailings heaps or tailings ponds. Sludge from hydrothermal gold processing in Minas Gerais, Brazil was found to contain 300-21,000 μg/g of As with a median of 10,500 μg/g (Matschullat, 2000). Elevated As concentrations in soils and sediments have also been attributed to arsenical pesticide and fertilizer use (Matschullat, 2000). Ironite, a commercial soil supplement and fertilizer derived from mining waste, has been found to contain 2800-6020 μg/g As (Dubey and Townsend, 2004). Anthropogenic activities and compositional differences in parent rocks control As distribution and result in a wide range of As concentrations in soils and sediments.

Natural processes play important roles in the transport and distribution of trace elements of both natural and anthropogenic origin. Various studies have documented how erosion by wind (e.g. Spencer et al., 1995) and water (e.g. Hill et al., 1997; De Carlo et al., 2004) can transport substances through the Hawaiian environment. The possibility of transport suggests the abundance of As in an area

may reflect the transport of materials from more distant sources as well as representing localized processes.

The mobility of arsenic is primarily determined by surface processes such as precipitation, dissolution, adsorption, and desorption. These processes are control by geochemical parameters such as pH, Eh, ionic composition, and mineral type (Bissen and Frimmel, 2003; Masscheleyn et al., 1991). At neutral pH and oxic conditions, As is effectively immobilized by adsorption or co-precipitated with metal oxides (Bissen and Frimmel, 2003; Smedley and Kinniburgh, 2002). Low pH and reduced redox potential increase As mobility by dissolution of metal oxides (Bauer and Blodau, 2006). The formation of sulfide minerals controls As concentrations in extremely reduced environments (Masscheleyn et al., 1991). Dissolved calcium enhances the sorption of arsenic while the presence of phosphate and other anions reduces sorption through competition for binding sites (Appelo et al., 2002; Smith et al., 2002).

1.2. Arsenic Toxicity

The toxicity of As is largely a function of its speciation. Unfortunately, data on the various forms of arsenic are limited. Generally, inorganic species are more toxic than organic species (Squibb and Fowler, 1983; NRC, 1999; Abernathy et al., 2003). Early research focused on arsenite (LD_{50} of about 10 mg/kg) which is more toxic than arsenate (LD_{50} of about 100 mg/kg) (Squibb and Fowler, 1983). Recently it has been reported that trivalent monomethylated and dimethylated metabolites of inorganic arsenic are more toxic than arsenite (Abernathy et al., 2003).

Most research concerning mechanisms of arsenic toxicity has been directed toward understanding the effects of arsenite and arsenate on biological systems. The main mechanism by which arsenite exerts its toxic effects is through reactions with protein sulfhydryl groups, resulting in inhibition of various enzyme systems (Squibb and Fowler, 1983). Arsenate toxicity is mainly derived from its chemical similarity to phosphate. Numerous studies have demonstrated that arsenate can compete with and substitute for phosphate in many enzyme catalyzed reactions, most notably in the production of adenosine diphosphate (ADP) (Squibb and Fowler, 1983). Many organisms convert more toxic inorganic As species to organic forms to avoid accumulation of lethal amounts (Cullen and Reimer, 1989).

Research documentation of As toxicity has encouraged many governing agencies to enforce environmental guidelines limiting As concentrations. Until recently, the US Environmental Protection Agency (EPA) enforced a Maximum Contaminant Level (MCL) of 50 μg/L of As in drinking water. In 2001, the MCL was lowered to10 μg/L on recommendations from the WHO based on increased awareness of its toxicity.

The Canadian Council of Ministers of the Environment (CCME) has proposed guidelines for freshwater and marine sediments and soils based on chronic exposure. CCME guidelines suggest that no greater than 12 μg/g As be present in soils regardless of land use. Freshwater sediment guidelines set the interim sediment quality guideline (ISQG) at 5.9 μg/L As while the probable effect level (PEL) is set at 17 μg/L As. Marine sediment guidelines set the ISQG at 7.24 μg/L As while the PEL is set at 41.6 μg/L As.

1.3. Environmental Setting of O'ahu, Hawai'i

O'ahu is the third largest island (1564 km^2) in the Hawaiian archipelago and is located between latitude 21˚15′ N and 21˚45′ N and longitude 158˚20′ W and 158˚35′ W in the north-central Pacific (Stearns, 1985). The Hawaiian archipelago is the youngest portion of the Hawaiian Ridge-Emperor Seamounts chain that extends roughly 6,000 km from the island of Hawai'i to the Aleutian Trench off Alaska as a result of the movement of the Pacific Plate over the Hawaiian mantle hotspot (MacDonald et al., 1983). Volcanic eruptions above the hotspot continuously form new land with volcanic activity focused at Kilauea Volcano along the East Rift Zone on the island of Hawai'i and at Lo'ihi Seamount 35 km off the southern coast of the Big Island (MacDonald et al., 1983).

The topography of O'ahu is shaped by the remnants of two shield volcanoes. The older Wai'anae Volcano in the west and the younger Ko'olau Volcano in the east formed roughly 3.9 Ma and 2.7 Ma, respectively (MacDonald et al., 1983). Millions of years of stream, wave and wind erosion on O'ahu have caused mass wasting of the shield volcanoes producing the landscape of steep basaltic mountains, deep valleys, and sheer interfluvial ridges seen today. The Wai'anae ranges reaches 1,226 m at its highest peak, Mt. Ka'ala, and the Ko'olau range reaches 919 m at its highest peak, Pu'u Kōnāhuanui (Stearns, 1985). The Schofield Plateau, the saddle located between the two mountain ranges, was formed by lavas from the Ko'olau Volcano banking against the older Wai'anae Volcano (Stearns, 1985). A coastal plain mainly composed of marine sediments and ancient reef deposited on basalt flows at time of higher sea level surrounds the island (Stearns, 1985).

The prevalent rock type in Hawai'i is tholeiitic basalt with a relatively uniform composition, especially when compared to the high degree of variability in rock types typical of continental settings. Although the overall composition of Hawaiian basalt is relatively narrow in range the trace element content can vary significantly (e.g. MacDonald et al., 1972; Frey et al., 1994). As a result of the olivine and pyroxene components, volcanic rocks characteristic of Hawai'i typically contain higher concentrations of certain transition elements than continental rocks (Frey et al., 1994; Kabata-Pendias, 2001). Some of these elements can become further concentrated during soil formation (Li, 2000).

Persistent northeasterly trade winds have a strong effect on local climate. The winds carry warm, moist air across the ocean where it encounters the steep windward mountain barrier and is forced to rise. The air cools adiabatically as it rises and its relative humidity increases. In most cases, the moisture condenses and precipitates on the windward side of the mountain. When the moisture-depleted air moves down the leeward side of the mountains, it warms and becomes relatively drier. As a result little precipitation reaches the leeward side of the mountains. This is reflected in the distribution of rainfall on O'ahu (Fig. 2). The greatest annual rainfall on the island occurs near the crest of the windward Ko'olau range and exceeds 700 cm (Giambelluca et al., 1984). In contrast, the maximum annual rainfall in the leeward Wai'anae range reaches just over 200 cm and the leeward coastal areas receive less than 60 cm annually (Giambelluca et al., 1984).

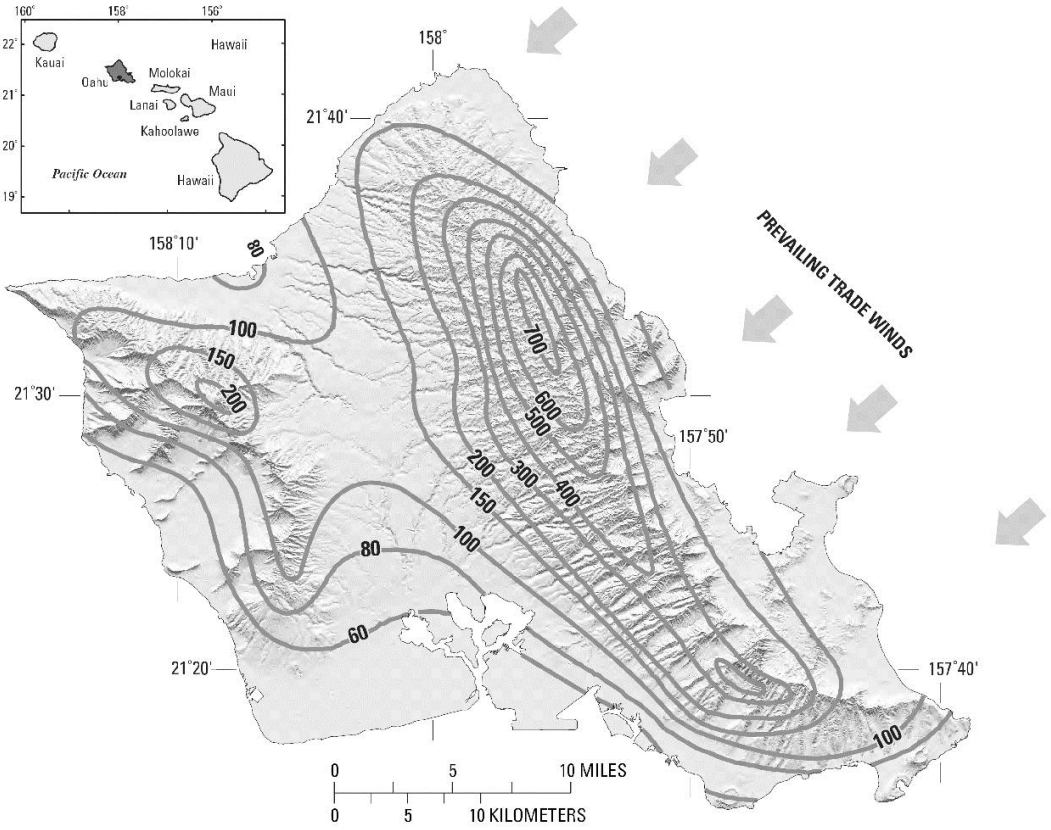

Figure 2. Map of the Hawaiian Islands showing elevation and annual rainfall on O'ahu. From Giambelluca et al. (1984). Isohyets in cm/a.

Located on SE O'ahu, Honolulu is one of the larger cities in the US, with a population of over 800,000 people recorded in the 2000 Census. According to Fulton et al. (2001), Honolulu has a population density of 3054 people/km^2, by far the highest of any US metropolitan area. Most of the population on the island lives in the coastal plain although Schofield Plateau has become increasingly urbanized since large scale pineapple and sugar cane plantation agriculture has ceased.

2. ANALYTICAL METHODS

2.1. Sample Collection and Preparation

A total of 56 soil and sediment samples were collected July 24, 2006 thru Sept 5, 2006 and April 14, 2007 thru May 27, 2007 on O'ahu, Hawai'i (Fig. 3). Sample locations were chosen to represent a variety of environments with varying degrees of human impact. Sample descriptions and location information can be found in Appendix A. Soils were sampled at depths ranging from 5 cm to 25 cm to avoid root structures and surface debris while beach sands were collected from the surface near the waterline. Sediment collected at each location was stored in quart Ziploc® bags. The samples were then dried in a laboratory oven at 60 °C to constant weight. Any large rocks, roots, plastics, and glass fragments present in the sample were removed. To ensure homogenization and allow dissolution, samples 1-31 were ground using a mortar and pestle and samples 32-56 were ground using a ball and mill grinder. The color of the dry ground samples was determined using a Munsell chart and recorded. Site and sample descriptions and relevant details can be found in Appendix A.

Subsamples of all soils and sediments weighing approximately 0.2 g (exact weight recorded to ± 0.1 mg) were digested in sealed vessels using a CEM MDS-2100 microwave digestion system with a slight modification of the microwave procedure described by De Carlo and Spencer (1995). Samples were digested in a strong acid solution containing 5 mL concentrated trace metal clean HNO_3, 2 mL concentrated trace metal clean HCl and 1 mL concentrated trace metal clean HF. Each digestion batch included a maximum of nine unique samples, one sample replicate, one certified reference material (CRM), and one reagent blank. Digestion

details can be found in Appendix B. After digestion, the acids were evaporated to near dryness and samples were re-dissolved and diluted with 2% HNO_3 to approximately 100 g (exact weight recorded) under a laminar flow hood using trace metal clean procedures. The sample solutions were further diluted tenfold with 2% HNO_3 immediately prior to analysis under a laminar flow hood using trace metal clean procedures.

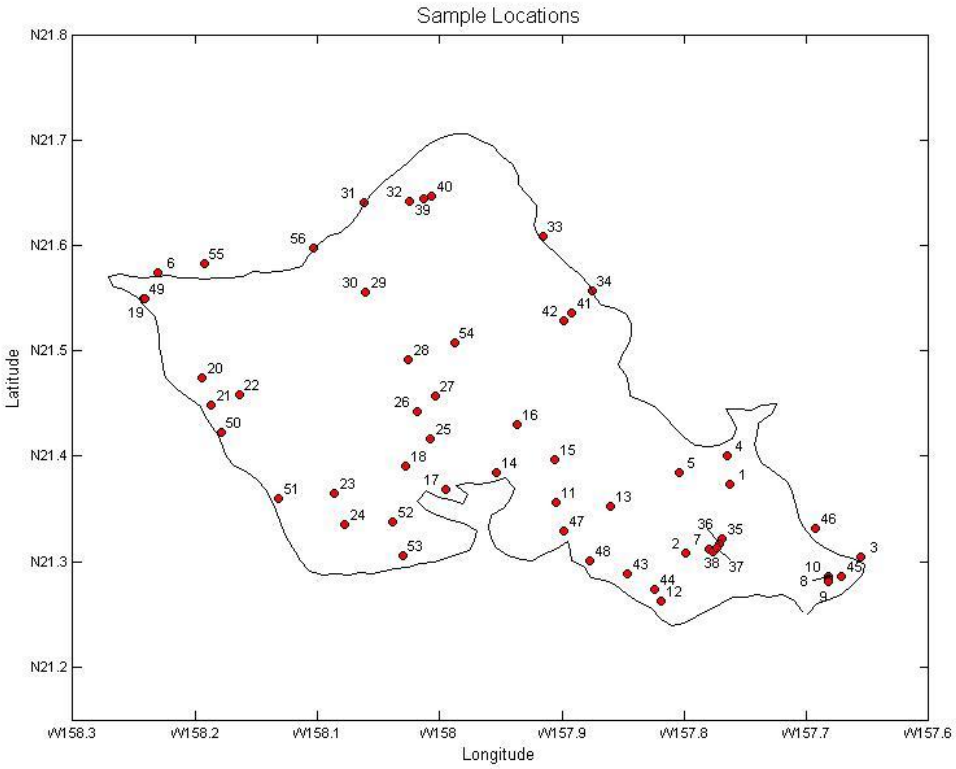

Figure 3. Map of soil and sediment sample locations on O'ahu, Hawai'i.

2.2. Sample Analysis by Inductively Coupled Plasma Mass Spectrometry

Inductively Coupled Plasma Mass Spectrometry (ICPMS) is a highly sensitive analytical method that utilizes inductively coupled plasma (ICP) as an ion source and a mass spectrometer as the ion filter and counter. Fig. 4 illustrates the basic

components of a quadrupole argon ICP mass spectrometer. The sample solution is introduced by an autosampling peristaltic pump into a nebulizer, where it is converted into an aerosol. The fine drops are separated from the larger drops in a spray chamber and injected into the plasma torch. The plasma is formed by the interaction of a strong magnetic field generated by passing radio frequency through a copper induction coil on a tangential flow of argon gas through concentric quartz tubes. This ionizes the gas and forms a very high temperature plasma, where temperatures can reach near 10,000 K, sufficient to cause a large fraction of the s ample to form ions. The ions are transported into the mass spectrometer through the interface region. The interface consists of two metal cones, the external sampler and internal skimmer cones, with holes between 0.6-1.2 mm in diameter, and is maintained at 1-2 Torr with a mechanical roughing pump. After supersonic expansion into the high vacuum region, the ions are guided by a series of lenses that focus an ion beam toward the mass separation device and inhibit photons, particulates and neutral species from reaching the detector. The lens chamber and mass separation device are kept at a vacuum of 10^{-6} Torr by two turbomolecular pumps. The quadrupole mass filter regulates the passage of ions to the detector with different voltage combinations and allows only analyte ions of a particular m/z ratio to pass. The detector converts the ions into an electrical signal from which analyte concentrations are calculated using the calibration standards.

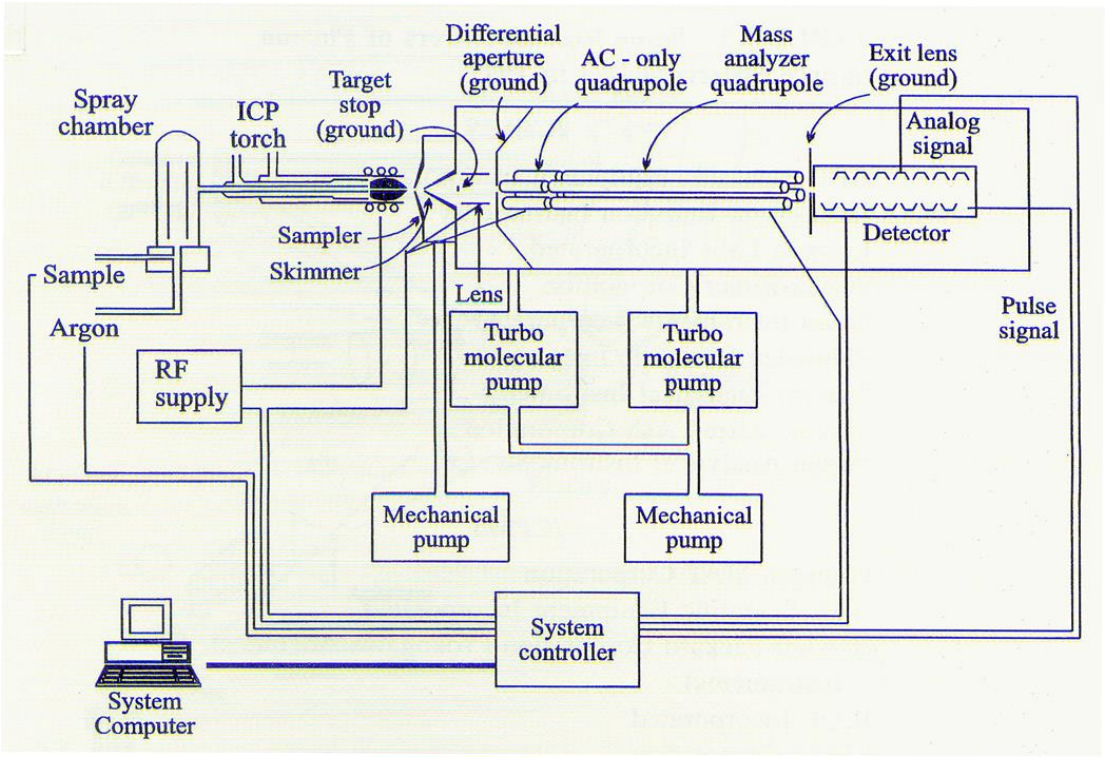

Figure 4. Schematic diagram of the basic components of a quadrupole argon ICP mass spectrometer. From Montaser (1998).

ICPMS allows reliable and rapid multi-element determinations of atomic masses ranging from 3-250 amu, with resolution of less than one amu at or below the ng/g level and up to eight orders of dynamic range (Thomas, 2004). The lack of magnetic fields in quadrupole ICPMS allows movement from mass to mass with high precision. This level of precision enables a technique known as "peak jumping" or "peak hopping" in which only one to a few points of data are acquired at the peak of each analyte. Operating the mass spectrometer using this technique greatly improves sensitivity relative to a scanning mode of operation.

Unfortunately, the lower resolution of the quadrupole ICP mass spectrometer results in molecular interferences that prohibit determinations at certain masses. For example, determination of ^{56}Fe is not feasible due to interference by $^{40}Ar\ ^{16}O^{+}$

molecular species easily formed in the plasma (Montaser, 1998). Interference introduced from the sample matrix or solvent by $^{40}Ar\ ^{35}Cl^{+}$ at mass 75 is possible and could potentially affect the determination of ^{75}As (Montaser, 1998). Other common interferences and the analyte isotopes affected are shown in Table 1 and Table 2.

Table 1. Common plasma/matrix/solvent-related spectral interferences in ICPMS.

Element isotope	Matrix/solvent	Interference
$^{39}K^{+}$	H_20	$^{38}ArH^{+}$
$^{40}Ca^{+}$	H_20	$^{40}Ar^{+}$
$^{56}Fe^{+}$	H_20	$^{40}Ar^{16}O^{+}$
$^{80}Se^{+}$	H_20	$^{40}Ar^{40}Ar^{+}$
$^{51}V^{+}$	HCl	$^{35}Cl^{16}O^{+}$
$^{75}As^{+}$	HCl	$^{40}Ar^{35}Cl^{+}$
$^{28}Si^{+}$	HNO_3	$^{14}N^{14}N^{+}$
$^{44}Ca^{+}$	HNO_3	$^{14}N^{14}N^{16}O^{+}$
$^{54}Mn^{+}$	HNO_3	$^{40}Ar^{15}N^{+}$
$^{48}TI^{+}$	H_2SO_4	$^{32}S^{16}O^{+}$
$^{52}Cr^{+}$	H_2SO_4	$^{32}S^{18}O^{+}$
$^{64}Zn^{+}$	H_2SO_4	$^{32}S^{16}O^{16}O^{+}$
$^{63}Cu^{+}$	H_2SO_4	$^{31}P^{16}O^{16}O^{+}$
$^{24}Mg^{+}$	Organics	$^{12}C^{12}C^{+}$
$^{52}Cr^{+}$	Organics	$^{40}Ar^{12}C^{+}$
$^{65}Cu^{+}$	Minerals	$^{48}Ca^{16}OH^{+}$
$^{64}Zn^{+}$	Minerals	$^{48}Ca^{16}O^{+}$
$^{63}Cu^{+}$	Seawater	$^{40}Ar^{23}Na^{+}$

From Thomas (2004)

Table 2. Elements that readily form oxides, hydroxides, hydrides and doubly charged species in the plasma and the analytes affected by the interference.

Analyte(s) Affected	Interference
$^{56}Fe^{+}$	$^{40}Ca^{16}O^{+}$
$^{64}Zn^{+}$	$^{48}Ti^{16}O^{+}$
$^{114}Cd^{+}$	$^{98}Mo^{16}O^{+}$
$^{154}Sm^{+}$, $^{154}Gd^{+}$	$^{138}Ba^{16}O^{+}$
$^{155}Gd^{+}$	$^{139}La^{16}O^{+}$
$^{156}Gd^{+}$, $^{156}Dy^{+}$	$^{140}Ce^{16}O^{+}$
$^{57}Fe^{+}$	$^{40}Ca^{16}OH^{+}$
$^{66}Zn^{+}$	$^{31}P^{18}O^{16}OH^{+}$
$^{80}Se^{+}$	$^{79}BrH^{+}$
$^{64}Zn^{+}$	$^{31}P^{16}O_2H^{+}$
$^{69}Ga^{+}$	$^{138}Ba^{2+}$
$^{69}Ga^{+}$	$^{139}La^{2+}$
$^{70}Ge^{+}$, $^{70}Zn^{+}$	$^{140}Ce^{2+}$

From Thomas (2004)

Efficient ion formation is necessary for high sensitivity in ICPMS. Thus, determination of elements with high first ionization potentials presents a challenge. The amount of energy required to generate Ar^{+} is 15.75 eV which is more than sufficient to ionize most other elements (Table 3). Differences in instrumental sensitivity between elements are in part due to differences in their first ionization potentials. Fig. 5 shows counts per second (CPS) detected by the mass spectrometer for As and Co in 0.5 ppb, 1.0 ppb, 2.5 ppb, 5.0 ppb, and 10.0 ppb multi-element calibration standards on July 2, 2007. Both As and Co are monoisotopic and have relatively close m/z, but they vastly differ in the CPS detected in each calibration standard. This demonstrates the decreased instrument sensitivity for elements with higher ionization potentials.

Table 3. First ionization potentials (eV) for selected elements.

Element	First Ionization Potential
Na	5.14
U	6.19
Pb	7.42
Cu	7.73
Co	7.86
Cd	8.99
Zn	9.39
As	9.79
P	10.49
Cl	12.97
O	13.62
Ar	15.75

From (CRC, 2007)

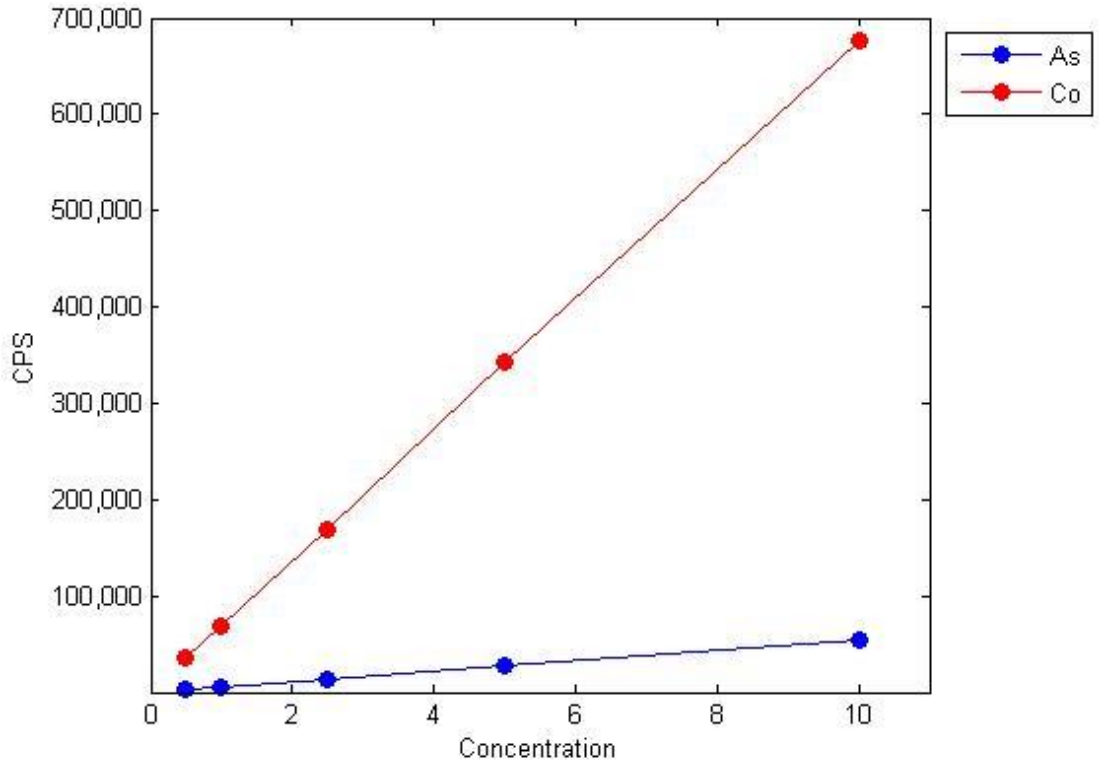

Figure 5. Counts per second detected by the mass spectrometer for As and Co in 0.5 ppb, 1.0 ppb, 2.5 ppb, 5.0 ppb, and 10.0 ppb multi-element calibration standards on July 2, 2007. A linear least squares regression is shown for each analyte.

The abundance of ^{59}Co, ^{65}Cu, ^{75}As, ^{111}Cd, ^{207}Pb, ^{208}Pb, and ^{238}U isotopes in the samples was determined by a VG PQ-2S quadrupole ICP mass spectrometer operated with Thermo Scientific PlasmaLab software. Prior to sample analysis, the instrument was tuned for maximum sensitivity using a 10 ppb solution containing ^{9}Be, ^{24}Mg, ^{59}Co, ^{115}In, ^{165}Ho, ^{208}Pb, ^{238}U. The tuning process involves adjusting the positioning of the plasma torch component and the various lenses of the instrument as well as adjusting the flow rate of the peristaltic pump and argon gas to obtain the highest count rate for each element. A mass calibration was run to allow the instrument to associate the voltage applied to the quadrupole with the ions of given masses. Short term stability was evaluated by ten sequential one minute analyses of a multi-element solution. The instrument was considered stable when the relative standard deviation was less than or equal to 2% for each mass of interest. Five aqueous multi-element standards containing 0.5 ppb, 1.0 ppb, 2.5 ppb, 5.0 ppb, and 10.0 ppb of all elements of interest were produced by dilutions of a 100 ppb SPEX ICPMS-2A mixed metal stock solution containing natural isotope abundances of Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, K, Li, Mn, Mg, Na, Ni, Pb, Rb, Se, Sr, Tl, U, V, and Zn. These solutions and a blank 2% HNO_3 solution were used for instrument calibration. Fig. 6 shows a calibration curve obtained on July 11, 2007 for ^{75}As.

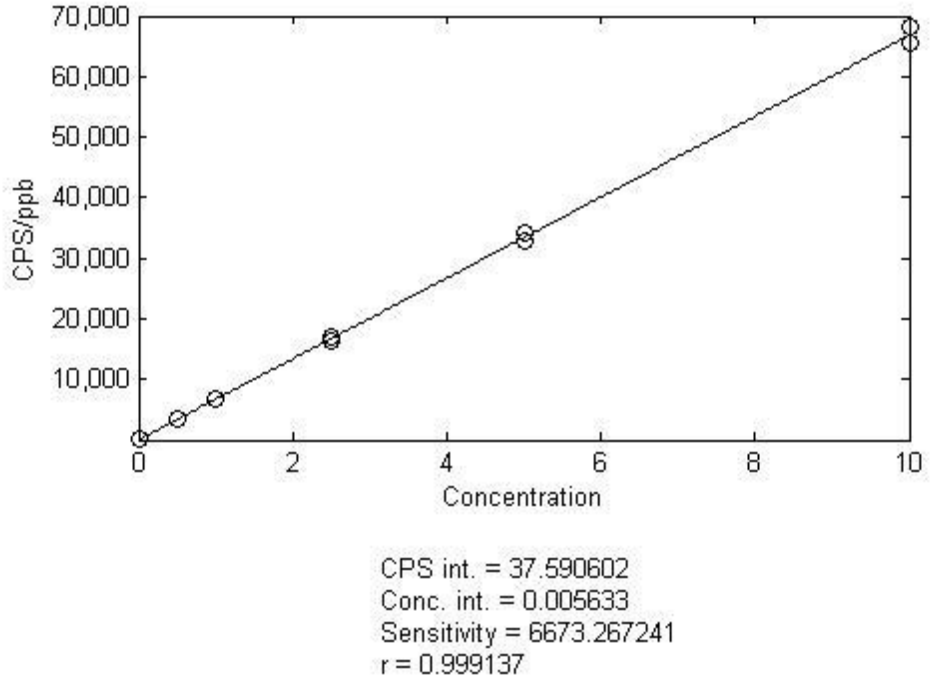

Figure 6. Calibration for As obtained on July 11, 2007.

The ICP mass spectrometer was operated in pulse-counting mode using a peak jumping technique. The instrument was set to perform 300 sweeps for each determination with an acquisition time of 40 s per sample run. Each sample solution was analyzed three times and a mean count rate was calculated for each isotope. A dilute HNO_3 solution was aspirated for 60 s between each sample to rinse any remaining sample. Ion counting was delayed 60 s to allow the sample signal to equilibrate in the mass spectrometer.

Instrument drift correction was achieved by monitoring the signal intensity of internal standards ^{115}In and ^{209}Bi and adjusting analyte signal intensities according to the measured signal intensities of the internal standards. Total trace element concentrations in the samples are calculated from the measured count rates at selected

isotope masses and assuming natural isotope abundances as present in the calibration standards.

2.3. Quality Assurance and Quality Control

Various methods were utilized to evaluate the quality of the ICPMS data. These included calculation of detection limits, calculation of signal reproducibility, and comparison of element concentrations measured in the CRM with certified values.

Detection Limits

The limit of detection (LOD) was calculated for each analyte to establish the quantifiable limit. The LOD is the amount of analyte that will produce a signal that is distinguishable from noise with 99% confidence. This is typically measured by analyzing standards that are nearly zero in concentration and then calculating the standard deviation (*s*) of the measurements. LODs were calculated for each day analysis was performed from the pooled *s* (see Eq. 1) of all 2% HNO_3 blanks analyzed. These daily limits were then averaged. In order to reduce the probability of a false nondetection, *s* is multiplied by three as shown in Eq. 2 (IUPAC, 1997).

$$s_{pooled} = \sqrt{\frac{\sum_{i=1}^{k}\left((n_i - 1)s_i^2\right)}{\sum_{i=1}^{k}(n_i - 1)}} \qquad (1)$$

$$LOD = 3(s_{pool}) \qquad (2)$$

The variable s_i represents the standard deviation, and n_i is the number of samples analyzed.

Short-term Reproducibility (Intra-day)

Reproducibility is a measure of the variation in signals recorded by the instrument while analyzing the same sample multiple times under the same conditions. The percent relative standard deviation (%RSD) was calculated for each of the three consecutive analyte determinations made for each solution of sample or CRM. Standards and 2% HNO_3 blanks were excluded. The minimum, maximum and mean %RSDs were calculated for each day analysis was performed. Samples with analyte concentrations below the LOD were excluded from this calculation.

Intermediate-term Reproducibility (Inter-day)

Instrument reproducibility is a measurement of the variation in determinations made from instrument signals obtained while analyzing the same sample solution under different conditions. A total of eleven samples were selected at random to be analyzed on two different days to assess the inter-day reproducibility of the determinations. The *s*, mean and %RSD were calculated for the three determinations made for each sample on each day of analysis. The mean %RSD was then calculated for each analyte.

Chemical Processing Reproducibility

Chemical processing reproducibility is a measurement of the variation in sample preparation procedures. It is evaluated by analyzing solutions prepared from different subsamples of a given sample under the same conditions. A total of seven sets of sample replicates were processed and analyzed to assess the quality of the chemical processing. The *s*, mean and %RSD were calculated for the mean determinations made for each subsample. The mean %RSD was then calculated for each analyte.

Accuracy

A CRM (NRC Canada: MESS-1, marine estuarine sediment) was processed repeatedly to assess the recovery of the digestion procedure and provide a measure of accuracy during sample analysis. Certified values for MESS-1 constituents are provided by NRC Canada based on results of determinations by at least two independent methods of analysis. One subsample of MESS-1 was processed with each digestion batch as described in Chapter 2, Section 1. Constituent concentrations determined in each subsample of MESS-1 by ICPMS were compared to the 95% confidence intervals (CI) certified by NRC Canada.

2.4. Data Analysis

Calculation of Element Concentrations in Samples

Analyte concentrations were determined in diluted sample solutions. In order to calculate element concentrations in the original solid, a calculation was performed according to Eq. 3 for each element determined in each sample and CRM.

(3)

This equation calculates the concentration in ppm, $conc_{s(ppm)}$, of the original sample from $conc_{aq(ppb)}$, the concentration in ppb measured by the ICP mass spectrometer, $weight_{aq(g)}$, the solution weight in g recorded after the digested sample was re-dissolved, and $weight_{s(g)}$, the dry sample weight in g of the sample before digestion. The tenfold dilution immediately prior to analysis is taken into account with a dilution factor of ten in the numerator. The equation is divided by 1000 to report concentrations in ppm instead of ppb.

Interelement Correlations

The As concentrations in each sample were plotted against corresponding Co, Cu, Cd, Pb, and U concentrations. To determine the strength and significance of any correlation, Pearson's correlation coefficient (r) and p-values were calculated between As concentrations and Co, Cu, Cd, Pb, and U. All data manipulations and calculations to determine interelement correlations were completed using Matlab 7.0.4. The Pearson's correlation coefficient was calculated using Eq. 4.

(4)

In this equation r_{xy} is the correlation coefficient between element concentrations *x* and *y*, *n* is the total number of samples analyzed, x_i and y_i are individual element concentrations for comparison, $\bar{x}$ and $\bar{y}$ are mean concentrations, and s_x and s_y are standard deviations. All *p*-values were calculated for testing the hypothesis of no correlation. Each *p*-value is the probability of getting a correlation as large as the observed value by random chance, when the true correlation is zero. The *p*-value is computed by transforming the correlation to create a *t*-statistic having *n*-2 degrees of freedom, where *n* is the number of samples. The confidence bounds are based on an asymptotic normal distribution of $\frac{1}{2}\log\left(\frac{(1+r)}{(1-r)}\right)$, with an approximate variance equal to $\frac{1}{(n-3)}$. These bounds are accurate for large samples when the data has a multivariate normal distribution.

Concentration Distribution Maps

The concentrations of trace elements in the soil and sediment samples were mapped using Matlab 7.0.4.

Land Use

Each soil sample site was categorized as originating from either agriculture, urban, forested (conservation) or mixed land use. Land use was categorized as

agriculture if systematic raising of plants or animals was conducted in the area. Land use was categorized as urban if the area was mainly residential or commercial (includes most parks). Undeveloped sites with little evidence of human impact were classified under forested land use. Sites with multiple land uses were classified as mixed (includes golf courses and areas in the flood plain of streams with agricultural inputs). Beach sands were placed in their own category. The land use classification of each site can be found in Table 4 and Appendix A.

A box plot of As concentrations in soils for each land use (agriculture, urban, forested/conservation, mixed) was made using Matlab 7.0.4. A separate box was plotted for the As concentrations of the beach sands. Lower and upper boundaries of the boxes represent 25^{th} and 75^{th} percentile values, respectively. The line within each box represents the median concentration. Lines extend from each box to the most extreme value within 1.5 times the interquartile range. The circles represent outliers that are more than 1.5 times the interquartile range.

3. RESULTS

3.1. Analyte Concentrations

The soils and sediments exhibit a wide range of trace element concentrations. Table 4 lists concentrations of elements Co, Cu, As, Cd, Pb and U in the soils and sediments collected from the sites shown in Fig. 3. Concentrations of Co ranged from 3.3-101.7 μg/g with a mean concentration of 39.7 μg/g and concentrations of Cu ranged from 2.7-374.2 μg/g with a mean concentration of 147.4 μg/g. The mean concentration of As was 11.1 μg/g with concentrations ranging from 0.3-59.6 μg/g. Concentrations of Pb ranged from 0.4-176.1 μg/g with a mean concentration of 18.2 μg/g and concentrations of U ranged from 0.3-5.0 μg/g with a mean concentration of 1.6 μg/g. Concentrations of Co, Cu, As and Cd span roughly two orders of magnitude while Pb concentrations span approximately three orders of magnitude. Concentrations of U are more tightly distributed and only span one order of magnitude. Table 5 lists the minimum, maximum, median and mean concentrations determined for each element.

The concentrations of As in the soils and sediments sampled listed in Table 4 are mapped in Fig. 7. The highest concentrations are found in the island's interior. The six highest As concentrations are found at Central Oahu Regional Park, Waikele (59.6 μg/g), Pupukea Paumalu Forest Preserve (44.5 μg/g), Kawailoa Forest Preserve, Wahiawa (43.9 μg/g), Neal Blaisdell Park, Waimalu (30.1 μg/g), Kipapa Community Park, Mililani Town (26.7 μg/g), and Waipio Soccer Complex (26.6 μg/g).

Concentrations of Co, Cu, Cd, Pb, and U in the soils and sediments sampled are mapped in Fig. 8. High concentrations of these elements are also found

in the island's interior. However, the distribution appears broader as high concentrations are also found in coastal areas.

Table 4. Trace element concentrations (µg/g dry weight) in soils and sediments from O'ahu, Hawai'i.

Site Description	Sample ID	Type[a]	Land Use[b]	Co	Cu	As	Cd	Pb	U
Maunawili Valley Park, Olomana	001	S	F	23.0	210	0.3	0.6	no data	0.5
Wa'ahila Ridge State Recreation Area	002	S	F	40.6	333	15.4	0.9	no data	2.0
Makapu'u Lighthouse Trailhead	003	S	M	58.8	141	3.5	0.8	no data	0.6
Kapa'a Quarry Road, Kawanui Marsh	004	S	M	32.0	202	5.8	1.0	no data	1.2
Ho'omaluhia Botanical Gardens, Kahua Lehua section	005	S	A	25.5	252	13.3	1.1	no data	2.5
Mokuleia climb spot	006	S	F	55.9	83.9	4.0	1.1	no data	1.3
Ka'au Crater Trail, Palolo Valley, Honolulu Watershed Forest Preserve	007	S	F	33.3	235	13.4	0.9	no data	2.4
Koko Crater Trail	008	S	F	64.1	98.6	1.2	0.4	no data	0.9
Koko Crater Trail	009	S	F	78.1	142	4.3	0.5	no data	0.3
Koko Crater Botanical Gardens, Hawaiian section	010	S	A	70.3	121	3.0	0.6	4.4	0.5
Salt Lake	011	S	M	29.6	189	19.6	0.7	21.1	5.0
Kapi'olani Park, Waikiki	012	S	U	52.1	103	8.1	1.5	115	1.1
Kupehau Park, Kalihi Valley	013	S	U	75.1	200	20.8	1.2	73.9	2.1
Neal Blaisdell Park, Waimalu	014	S	M	102	268	30.1	2.1	29.6	2.7
Keaiwa Heiau State Recreation Area, Aiea Heights	015	S	F	29.1	196	19.1	0.8	28.8	1.7
Manana Trail, Pacific Palisades	016	S	F	25.6	238	2.7	0.9	6.3	1.7
Waipio Soccer Complex	017	S	M	77.3	215	26.6	1.4	15.6	2.9
Hoaeae Community Park, Village Park	018	S	U	22.6	163	1.7	0.7	3.4	0.7
Kaena Point State Park, Yokohama Bay	019	S	F	49.3	89.2	9.2	1.1	6.6	1.2
Makaha Valley Country Club	020	S	M	75.0	143	4.9	0.8	5.6	0.8
Waianae Pilia'au Field	021	S	U	48.5	114	8.1	0.6	6.8	0.8
Kaupuni Neighboorhood Park, Waianae Homesteads	022	S	U	23.0	225	17.5	0.7	14.3	2.3
Makakilo Community Park	023	S	U	45.6	137	3.8	0.7	19.3	1.2
Kapolei Regional Park	024	S	U	94.6	223	16.8	1.3	7.8	1.5
Central Oahu Regional Park, Waikele	025	S	M	92.1	328	59.6	3.5	18.1	2.1

Table 4 (continued). Trace element concentrations (µg/g dry weight) in soils and sediments from O'ahu, Hawai'i.

Site Description	Sample ID	Type[a]	Land Use[b]	Co	Cu	As	Cd	Pb	U
Mililani District Park	026	S	U	61.3	234	9.1	1.5	9.0	1.7
Kipapa Community Park, Mililani Town	027	S	U	99.1	279	26.7	0.8	31.2	2.8
Wahiawa Freshwater State Park	028	S	U	37.1	340	16.8	0.9	20.5	1.5
Pineapple fields, Kamehameha Highway 99, A	029	S	A	99.4	374	21.8	1.6	176	2.2
Pineapple fields, Kamehameha Highway 99, B	030	S	A	73.0	170	12.6	0.7	28.1	0.9
Waimea Beach	031	B	B	7.1	5.5	5.1	0.2	0.4	1.1
Pupukea Paulmalu Forest Preserve	032	S	F	56.0	178	44.5	0.6	42.1	1.8
Hau'ula Forest Preserve	033	S	F	73.9	184	10.6	0.4	3.0	0.4
Kahana Bay Beach	034	B	B	16.4	18.1	16.8	0.3	5.0	2.5
Mau'umae Trail, Mau'umae Ridge, Honolulu Watershed Preserve	035	S	F	16.9	189	7.9	1.2	11.9	1.3
Mau'umae Trail, Mau'umae Ridge, Honolulu Watershed Preserve	036	S	F	15.9	163	5.8	0.3	7.6	0.8
Mau'umae Trail, Mau'umae Ridge, Honolulu Watershed Preserve	037	S	F	8.1	55.2	2.1	1.4	10.4	0.4
Mau'umae Trail, Mau'umae Ridge, Honolulu Watershed Preserve	038	S	F	38.6	246	1.4	0.4	1.6	0.5
Kaunala Trail, Pupukea Paumalu Forest Preserve	039	S	F	19.0	182	8.2	0.6	16.5	1.2
Kaunala Trail, Pupukea Paumalu Forest Preserve	040	S	F	81.1	253	2.3	0.5	3.7	0.5
Nakoa Trail, Kahana Valley	041	S	F	19.0	181	20.4	0.9	19.6	2.6
Nakoa Trail, Kahana Valley	042	S	F	32.1	201	6.6	0.6	10.4	1.2
Ala Moana Beach Park	043	B	B	4.7	5.4	2.0	0.1	2.9	1.2
Kuhio Beach, Waikiki	044	B	B	4.4	3.1	2.6	ND	1.7	1.3
Sandy Beach Park	045	B	B	12.2	4.1	3.0	ND	3.0	1.3
Waimanalo Beach Park	046	B	B	7.6	2.7	2.7	ND	1.4	1.9
Ke'ehi Lagoon Beach Park	047	B	B	4.4	6.7	2.1	0.1	2.7	1.9
Sand Island State Park	048	B	B	3.9	7.1	5.1	0.1	22.3	2.1
Ka'ena Point State Park, Yokohama Bay	049	B	B	8.3	7.3	2.8	0.1	3.8	1.3
Maili Beach Park	050	B	B	3.3	3.9	2.5	0.1	1.4	1.5

Table 4 (continued). Trace element concentrations (µg/g dry weight) in soils and sediments from O'ahu, Hawai'i.

Site Description	Sample ID	Type[a]	Land Use[b]	Co	Cu	As	Cd	Pb	U
Kahe "Tracks" Beach Park	051	B	B	6.9	6.1	3.3	0.1	1.2	1.6
Ewa Mahiko District Park	052	S	U	54.8	112	7.9	0.9	10.7	1.3
One'ula Beach Park, Ewa	053	B	B	4.8	4.1	2.1	ND	3.9	1.9
Kawailoa Forest Preserve, Wahiawa	054	S	F	15.9	165	43.9	1.0	24.6	4.2
Mokuleia Beach Park	055	B	B	4.4	14.1	2.7	ND	1.5	1.1
Haleiwa Beach Park	056	B	B	12.5	13.0	6.1	0.1	2.9	1.5

[a] B - beach sand, S - soil

[b] A - agriculture, U - urban, F - forested, M - mixed, B - beach sand

Abbreviations: ND, not detected

Table 5. Summary of results: minimum, maximum, median and mean concentrations (µg/g dry weight) of elements in soils and sediments measured by ICPMS.

Element Measured	Minimum Concentration	Maximum Concentration	Median Concentration	Mean Concentration
Co	3.3	101.7	32	39.7
Cu	2.7	374.2	163.8	147.4
As	0.3	59.6	6.4	11.1
Cd	below LOD	3.5	0.7	0.7
Pb	0.4	176.1	7.8	18.2
U	0.3	5.0	1.3	1.6

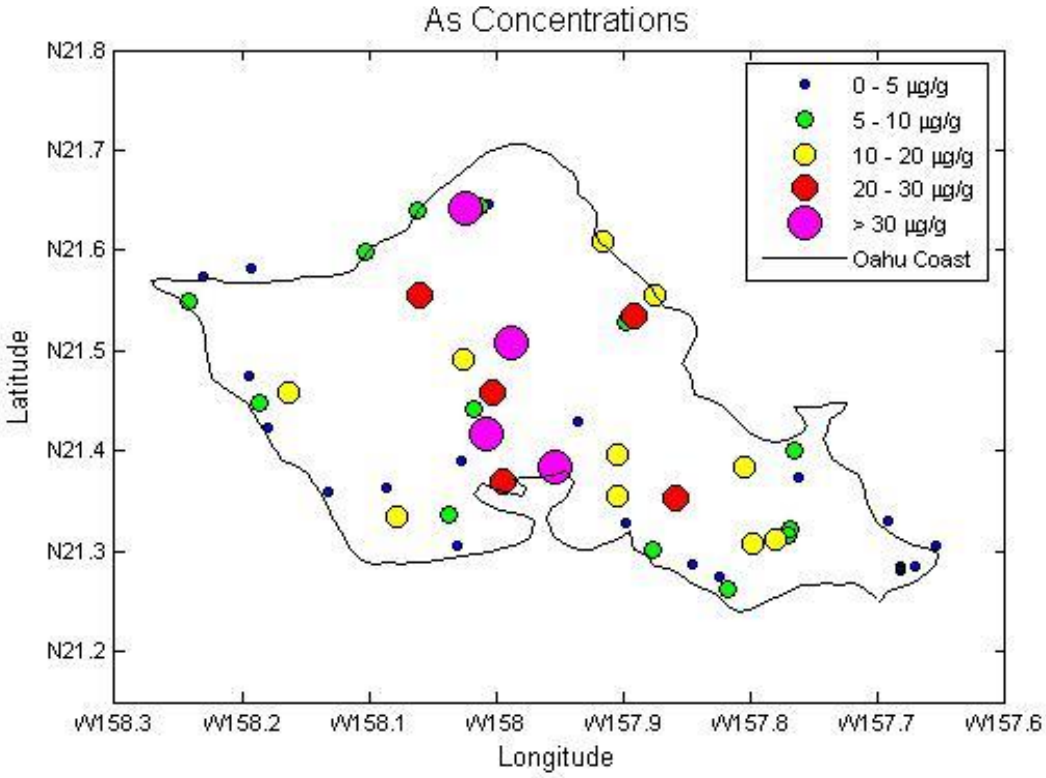

Figure 7. Map of O'ahu showing As concentrations at each sample location.

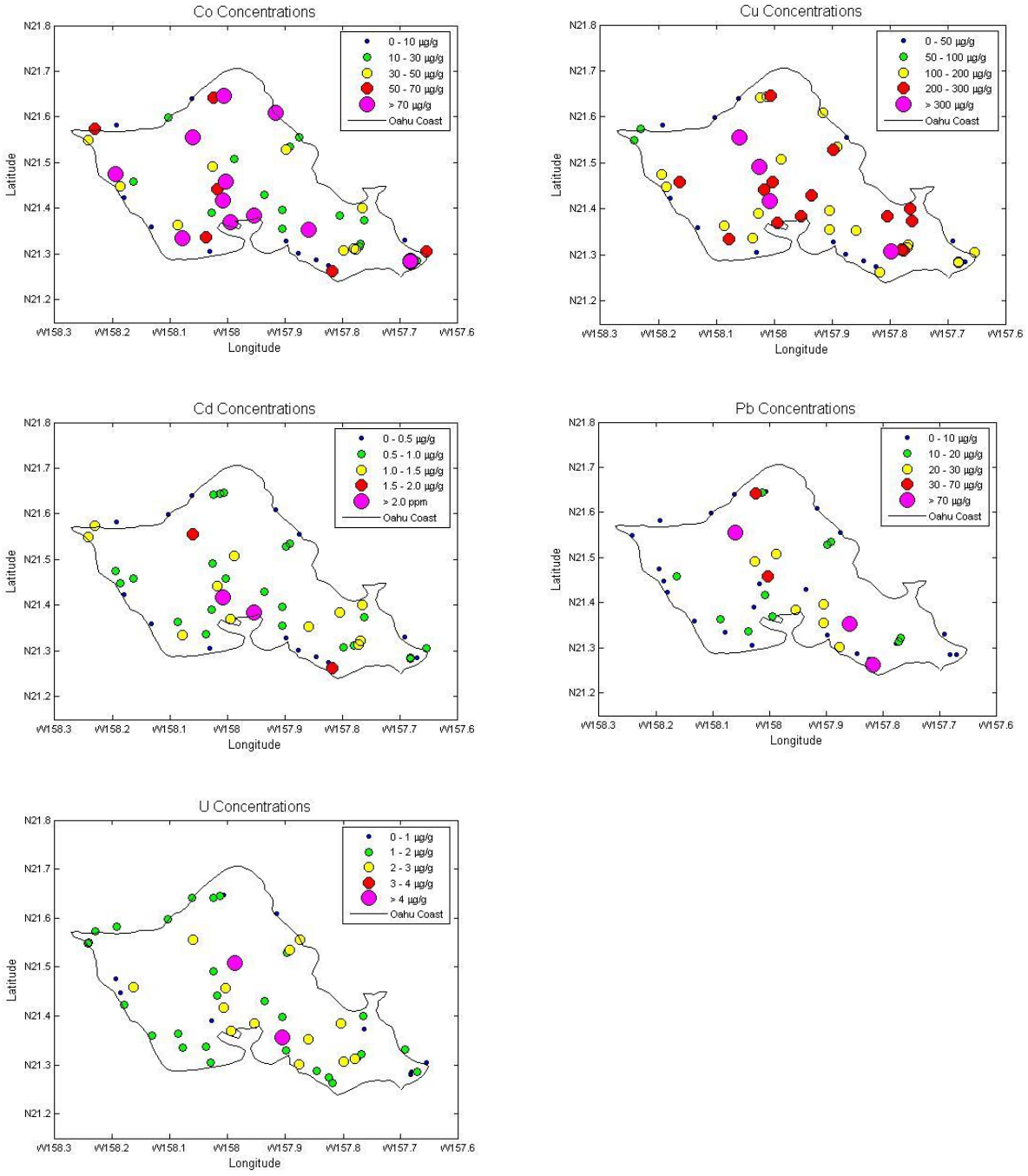

Figure 8. Map of O'ahu showing Co, Cu, Cd, Pb, and U concentrations at each sample location.

3.2. Quality Assurance and Quality Control

Detection Limits

Table 6 lists the average LODs for each element calculated using Eq. 2. LODs range from 0.001-0.014 μg/g, with U having the lowest LOD and Cu having the greatest LOD. The LOD for As is 0.009 μg/g.

Table 6. LOD (μg/g) for each element analyzed.

Element	Detection Limit
Co	0.003
Cu	0.014
As	0.009
Cd	0.005
Pb	0.005
U	0.001

Short-term Reproducibility (Intra-day)

The minimum, maximum and mean %RSDs for three consecutive determinations of each analyte in all samples and CRMs on each day the analysis was performed are listed in Table 7. The %RSDs for ^{111}Cd were consistently the highest. The %RSDs for ^{59}Co, ^{65}Cu, and ^{208}Pb were the lowest followed by the %RSDs for ^{75}As and ^{238}U. The data presented in Table 7 represent repeatability over a wide range of analyte concentrations. The %RSD values deteriorated significantly where analyte concentrations approached the LOD. Analysis on May 16, 2007 was performed in peak scanning mode, which is less sensitive than the peak hopping mode used during subsequent days of analysis. This difference likely accounts for the higher maximum %RSDs recorded for determinations made on this day.

Table 7. Minimum, maximum and mean %RSD for three consecutive determinations of each analyte in sample and CRM solutions by the day the analysis was performed.

		^{59}Co	^{65}Cu	^{75}As	^{111}Cd	^{208}Pb	^{238}U
5/16/2007*	Min. %RSD	0.67	0.42	0.67	0.52	0.90	1.21
	Max. %RSD	4.34	4.58	33.92	19.08	6.64	19.34
	Mean %RSD	2.11	2.09	6.35	6.02	2.41	5.78
6/4/2007	Min. %RSD	0.06	0.05	0.28	0.75	0.05	0.07
	Max. %RSD	2.10	1.93	2.99	8.71	2.35	4.02
	Mean %RSD	0.54	0.64	1.14	3.49	0.56	1.02
7/2/2007	Min. %RSD	0.23	0.35	0.34	0.34	0.16	0.22
	Max. %RSD	4.36	3.89	6.47	158.60	3.19	2.73
	Mean %RSD	1.49	1.14	2.14	19.33	1.07	1.39
7/11/2007	Min. %RSD	0.10	0.06	0.24	0.78	0.06	0.15
	Max. %RSD	5.90	8.80	2.62	33.97	2.26	2.98
	Mean %RSD	1.07	1.02	1.19	8.16	0.70	1.19
Average	Min. %RSD	0.27	0.22	0.38	0.60	0.29	0.41
	Max. %RSD	4.17	4.80	11.50	55.09	3.61	7.27
	Mean %RSD	1.30	1.22	2.71	9.25	1.19	2.35

* analysis performed in peak scanning mode

Intermediate-term Reproducibility (Inter-day)

A total of eleven individual samples were chosen at random and analyzed on two different days. The mean of the %RSD for each analyte determined in the same sample solution analyzed on different days is listed in Table 8. The mean %RSD for ^{111}Cd is by far the highest at 24.80. This is most likely due the combined effect of the extremely low Cd concentrations and the use of an isotope whose natural abundance is only 12.8% of the total Cd abundance. Excluding ^{111}Cd, all RSDs are below 7%.

Table 8. Mean %RSD for each analyte determined in sample solutions analyzed on two different days.

Element	Mean %RSD
^{59}Co	5.58
^{65}Cu	5.84
^{75}As	2.21
^{111}Cd	24.80
^{208}Pb	2.12
^{238}U	6.11

Chemical Processing Reproducibility

The mean %RSD for each analyte determined in two individually processed subsample solutions of seven samples analyzed is listed in Table 9. The sample replicate from digestion 6 was excluded from this calculation because of inconsistencies in sample uptake rate during its analysis. The mean %RSD for ^{111}Cd is the highest at 17.14 followed by ^{208}Pb at 10.27. Excluding ^{111}Cd and ^{208}Pb, all RSDs are below 4%.

Table 9. Mean %RSD for each analyte determined in subsample solutions of the same sample.

Element	Mean %RSD
^{59}Co	3.71
^{65}Cu	3.00
^{75}As	3.53
^{111}Cd	17.14
^{208}Pb	10.27
^{238}U	3.30

Accuracy

Element concentrations measured in all MESS-1 subsample solutions are compared to the certified mean and 95% CI in Table 10. Concentrations listed in bold fell outside the 95% CI of the certified mean. Determinations for Cu and Cd in all CRM processed fell outside the 95% CI of the certified mean. Measured Cu concentrations were systematically higher than the upper bound of the 95% CI of the certified mean. Mineral interferences for ^{65}Cu (e.g. $^{48}Ca^{16}OH$) are relatively common and may account for the difference between determined concentrations and the certified values (see Table 10). Measured Cd concentrations were also higher than the upper bound of the 95% CI of the certified mean. The high measured Cd concentrations may be a result of background noise since concentrations were near the LOD.

3.3. Interelement Correlation and Significance

Scatter plots of As concentration versus Co, Cu, Cd, Pb, and U concentrations for each sample are show in Fig. 9. Arsenic shows a positive correlation with all elements analyzed with *r* ranging from 0.3219 to 0.6467. The highest *r* occur when As concentrations are compared to Cd (0.6467) and U (0.5994) concentrations. All *p*-values are less than 0.05 and indicate the results are statistically significant at a 95% confidence level.

Table 10. Comparison of ICPMS determinations for MESS-1 subsample element composition with NRC Canada certified values. Concentrations listed in bold fall outside the 95% CI of the certified mean.

	Co	Cu	As	Cd	Pb	U[a]
CRM MESS-1 Mean	10.8	25.1	10.6	0.59	34	5
CRM MESS-1 95% CI	10.8 +/- 1.9	25.1 +/- 3.8	10.6 +/- 1.2	0.59 +/- 0.1	34 +/- 6.1	none
Mean of D1-Mess	10.8	**37.0**	**8.6**	**1.29**	no data	3.80
Mean of D2-Mess	9.2	**31.9**	10.2	**1.14**	39.8	4.10
Mean of D3-Mess	10.8	**37.1**	10.8	**0.80**	39.2	3.39
Mean of D4-Mess	10.4	**32.2**	10.3	**0.80**	32.5	3.19
Mean of D5-Mess	10.4	**30.0**	10.1	**0.86**	33.0	3.38
Mean of D6-Mess	9.9	**34.7**	10.7	**0.97**	35.0	3.44
Mean of D7-Mess	10.4	**35.1**	11.3	**0.86**	34.7	3.45
Mean of D8-Mess	10.9	**32.4**	10.5	**0.90**	32.5	3.21
Overall Mean	10.4	**33.8**	10.3	**0.95**	35.2	3.50

[a] not certified, value provided is semiquantitative

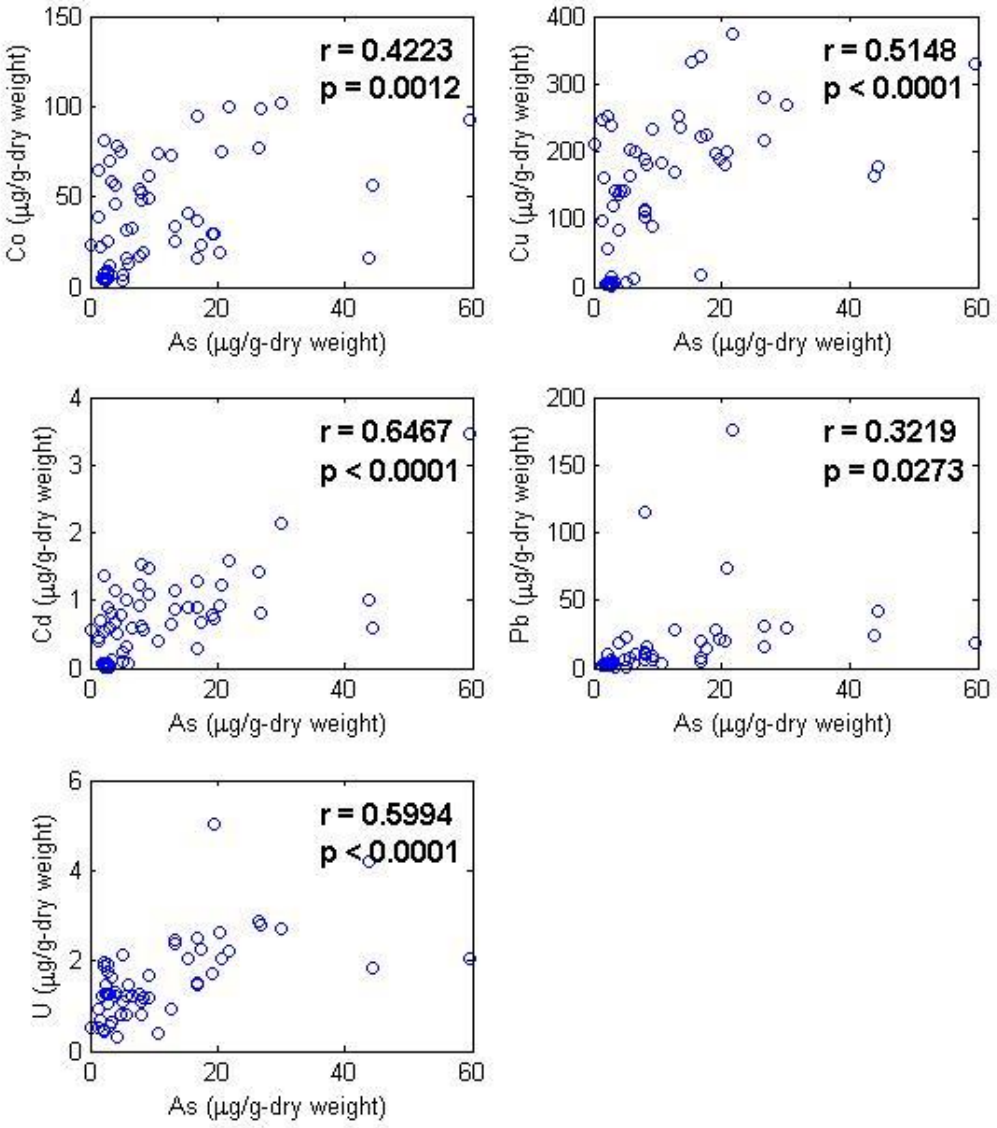

Figure 9. Scatter plots of As concentrations versus Co, Cu, Cd, Pb, and U concentrations. Pearson's correlation coefficients (r) and p-values are listed.

4. DISCUSSION

Concentrations of trace elements in soils and sediments are affected by inputs from both natural and anthropogenic sources. Understanding variations in trace element concentrations requires investigation of potential sources and their composition. A number of methods have been developed to reveal trace element sources. In this research, correlation between As and Co, Cu, Cd, Pb and U concentrations was evaluated (see Fig. 9 for results). Additionally, trace element concentrations are examined with respect to the dominant land use of the sample site location.

4.1. Interelement Correlations

A strong correlation between the concentrations of two elements suggests a common source. For instance, it is expected that the correlation between concentrations of Na and Cl in soils and sediments from coastal areas would be strong since sea spray is a source of both elements. Elements with no correlation indicate an origin from different sources. This approach is complicated by elements with multiple sources and sources that contribute trace elements in similar compositions. In these cases, interpretation of correlation becomes much more difficult.

As mentioned previously, the highest *r* occur when As concentrations are compared to Cd (0.6467) and U (0.5994) concentrations. Principal component analysis of trace element concentrations in SPM collected from streams in several watersheds on O'ahu, Hawai'i by De Carlo et al. (2004) shows As, Cd and U to be grouped into the same factor interpreted to represent agricultural inputs. The strong

correlation between these elements in this research further supports this interpretation.

4.2. Variation in Arsenic Abundance with Land Use

Soils and sediments collected in this research exhibit concentrations of As between 0.3 and 59.6 μg/g. A box plot of As concentrations in soils for each land use is presented in Fig. 10. Soils from areas of mixed land use have the highest and widest range of concentrations with a median As concentration of 19.6 μg/g (mean 21.4 μg/g) and are followed by those from agricultural areas with a median As concentration of 13.0 μg/g (mean 12.7 μg/g). Soils collected from urban areas have a median As concentration of 9.1 μg/g (mean 12.5 μg/g). Soils from forested (conservation) lands have the lowest and narrowest range of As concentrations with a median As concentration of 7.2 μg/g (mean 11.2 μg/g). Beach sands have even lower As concentrations with a median As concentration of 2.8 μg/g (mean 7.0 μg/g). The difference between soils and sands may be a result of the higher amount of binding sites available to scavenge As in the iron oxide rich soils typical of Hawai'i (Kabata-Pendias, 2001).

Results from this work differ from As concentrations measured in streambed sediments from various watersheds on O'ahu, Hawai'i. Table 11 lists the mean, minimum, and maximum As concentrations by land use as reported in this work along with those reported by De Carlo et al. (2005) in the O'ahu USGS NAWQA study. De Carlo et al. (2005) report As concentrations of a similar range varying from 1-44 μg/g. However, the highest As concentrations were associated with agricultural land use (mean 22 μg/g) and followed by those associated with mixed land use (mean

11.8 µg/g). Sediments associated with urban land use contained a mean As concentration of 8.1 µg/g and those from forested areas contained a mean As concentration of 1.5 µg/g.

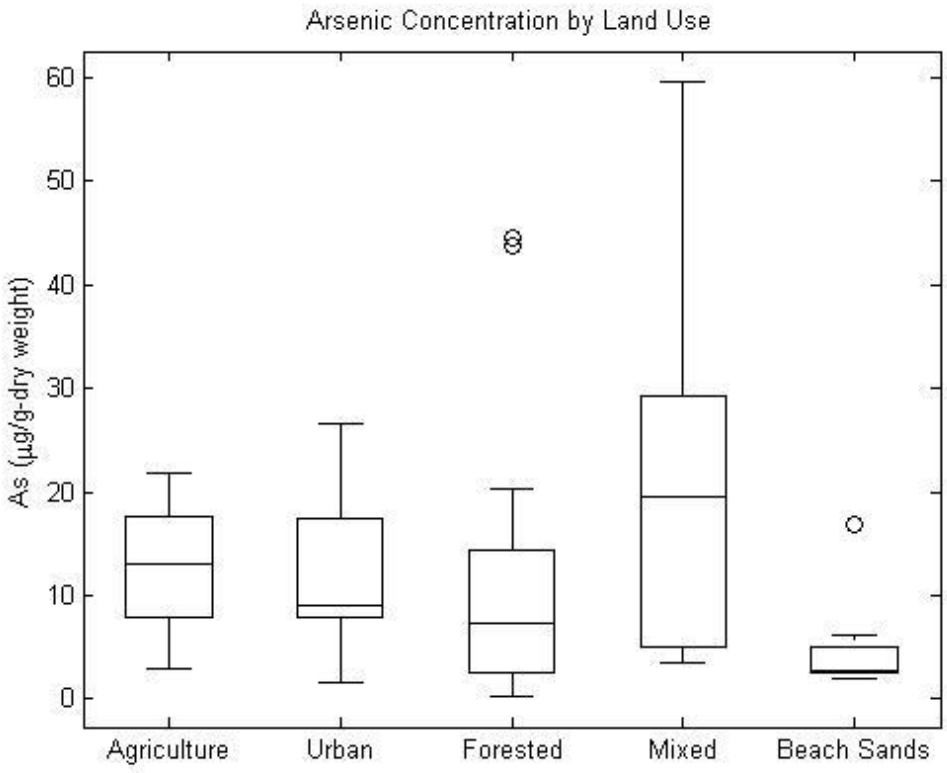

Figure 10. Box plot of As concentrations in soils from O'ahu, Hawai'i as a function of land use (agriculture, urban, forested/conservation, mixed). Beach sands are placed in a separate category. Lower and upper boundaries of the boxes represent 25th and 75th percentile values, respectively. The line within each box represents the median concentration. Lines extend from each box to the most extreme value within 1.5 times the interquartile range. The circles represent outliers that are more than 1.5 times the interquartile range.

Differences in As concentrations between those measured in this research and those measured in streambed sediments (De Carlo et al., 2005) from areas of agricultural land use may be a function of the sampling method employed in this research. All soils samples were collected below the humus layer, if present, to avoid

excessive organic matter that complicates the digestion procedure. The humus layer of soils acts as a natural biogeochemical barrier that suppresses the percolation of As with water and strongly accumulates the element (Goldschmidt, 1958). Accordingly, the highest As concentrations are typically found in soils rich in organic carbon. This surface organic matter would likely contain a majority of the As input from agricultural practices (pesticide and fertilizer use) and would be included from the suspended particulate load of a stream. Additionally, the current land use classification methods do not account for previous land use or material transfer between areas of different land use. Concentrations of arsenic reported for each land use category have a large range and may contain anomalous results. This is supported by lower median As concentrations than the mean As concentrations for each land use category. Each of these factors contributes to difficulties in clearly identifying trace element sources.

Table 11. Soil and sediment As concentrations (µg/g dry weight) compared with USGS NAWQA streambed sediment concentrations.

Land Use		This study	USGS NAQWA[a]
Agriculture		(n = 4)	(n = 3)
	Mean	12.7	22.0
	Max.	21.8	28.0
	Min.	3.0	16.0
	s	7.7	4.9
Urban		(n = 11)	(n = 5)
	Mean	12.5	8.1
	Max.	26.7	16.0
	Min.	1.7	2.4
	s	7.7	4.9
Forested		(n = 20)	(n = 6)
	Mean	11.2	2.4
	Max.	44.5	6.0
	Min.	0.3	1.0
	s	7.7	1.9
Mixed		(n = 7)	(n = 10)
	Mean	21.4	11.8
	Max.	59.6	44.0
	Min.	3.5	4.1
	s	20.0	12.8

[a] From De Carlo et al. (2005)

Abbreviations: n, number of samples; *s*, standard deviation

4.3. Comparison of O'ahu Arsenic Concentrations with Other Geochemical Data and Environmental Guidelines

In general, As concentrations in the soils and sediments from O'ahu, Hawai'i are higher than those found in other areas of the world. Table 12 lists trace element concentrations for selected materials. Reference geochemical data represent natural levels and should be compared with results from uncontaminated areas only. Soils from areas of forested (conservation) land use were found to have mean As concentrations of 11.2 µg/g which is higher than the world average and mean As concentrations reported for most other parts of the world. Median As concentrations may better represent the results in this research by placing less weight on

measurements that may be anomalous. The median As concentration for areas of forested land use is 7.2 µg/g which corresponds well with the mean As concentration of 7 µg/g for US soils.

Table 12. Trace element concentrations (µg/g dry weight) for selected rocks, soils and sediments.

	Co	Cu	As	Cd	Pb
US stream sediments, median[a]		27	6.3	0.4	27
US stream sediments, max.[a]		620	200	56	6,300
US stream sediments, min.[a]		6	1	<0.1	<4.0
Kaua'i basalts[b]	90	290	ND	ND	12
Kaua'i saprolites (<20 ft BLS)[b]	18	33	ND	ND	0.5
Mafic rocks (basalts, gabbros)[c]			0.6 – 2.0		
Bulk continental crust[d]	29	75	1	0.098	8
Upper continental crust[d,e]	14	25	1.5	0.1	18
US soils, mean[c]			7		
Canada soils, mean[c]			5.8		
Great Britain soils, mean[c]			16.3		
Norway soils, mean[c]			2.5		
Japan soils, mean[c]			11		
World soils[f]	10	5 – 20	5	<1.0	2 – 200
World avg. river susp. part.[d]	20	100	5	1	100

[a] Rice (1999)

[b] Patterson (1971)

[c] Kabata-Pendias (2001)

[d] Li (2000)

[e] Mean of two values provided by Li (2000)

[f] Pais and Jones (1997)

Abbreviations: BLS, below land surface; MORB, mid-ocean ridge basalts; ND, none detected; susp. part., suspended particulates; blank, no data available

Environmental Quality Guidelines (EQG) for soils and sediments proposed by the CCME are presented in Table 13. The mean As concentration in soils from forested (conservation) land use areas (11.2 µg/g) falls just below the soil CCME EQG of 12 µg/g. However, the mean As concentrations in soils from all other land uses exceed the CCME EQG. A total of 18 out of 42 or 42.9% of soil samples collected in this research exceed the CCME EQG for As. The mean As concentration

in beach sands (μg/g) falls below the CCME EQG for Marine ISQG of 7.24 μg/g. Only 1 out of 14 or 7.1% of beach sand samples collected in this research exceed the CCME EQG for As.

Table 13. CCME EQG for trace element concentrations (mg/kg dry weight) in various mediums.

	Co	Cu	As	Cd	Pb
CCME EQG freshwater and marine sediment quality guidelines					
Freshwater ISQG		35.7	5.9	0.6	35
Freshwater PEL		197	17	3.5	91.3
Marine ISQG		18.7	7.24	0.7	30.2
Marine PEL		108	41.6	4.2	112
CCME EQG soil quality guidelines					
Agricultural land use	40	63	12	1.4	70
Residential/park land uses	50	63	12	10	140
Commercial land uses	300	91	12	22	260
Industrial land uses	300	91	12	22	600

From Canadian Council of Ministers of the Environment (2002)

Abbreviations: EQG, environmental quality guideline; ISQG, interim sediment quality guideline; PEL, probable effect level; blank, no data available

The CCME EQG are proposed with the purpose of preventing adverse effects on biota from elevated concentrations of contaminants. In light of this, it is important to remember that much of the As measured in the samples collected may not be bioavailable. The sample digestion methods employed in this research are much more efficient at extracting As from soils and sediments than most organisms and only a fraction of the total arsenic will be bioavailable. Furthermore, As toxicity is highly dependent on speciation. This research involved no determination of As species and all data presented are for total As concentrations.

5. CONCLUSION

Soils and sediments samples were collected on O'ahu, Hawai'i from a variety of environments with varying degrees of human impact. Samples were classified as originating from areas of forested (conservation), agricultural, urban, or mixed land use and then dried, ground, and digested in a strong acid solution. Concentrations of Co, Cu, As, Cd, Pb, and U were measured using quadrupole ICPMS. Concentrations of As in all soils and sediments were found to range from 0.3 – 59.6 μg/g with a mean concentration of 11.1 μg/g. Soils from areas of mixed land use displayed the widest range and highest median As concentration of 19.6 μg/g. Soils from areas of agricultural land use displayed the next highest median As concentration of 13.0 μg/g. Soils from areas of urban land use have a median As concentration of 9.1 μg/g and soils from areas of forested (conservation) land use have a median As concentration of 7.2 μg/g. The beach sands collected had the lowest median As concentration of 2.8 μg/g, which may be due to the lack of binding sited available on carbonate materials in comparison to the iron oxide rich soils typical of Hawai'i. Strong correlation between measured concentrations of As, Cd, and U suggest the origin of As enriched in the soils and sediments analyzed to be derived from agricultural activity and is supported by previous research.

Concentrations of As measured in this research are generally higher than As concentrations previously measured in streambed sediments from O'ahu, Hawai'i, regardless of land use. However, mean As concentrations from areas of agricultural land use are lower than those previously reported in streambed sediments. This may be due to sample collection methods that involved removal and exclusion of the

humus layer from the sample. This mainly organic surface layer has been shown to strongly accumulate As and is a likely location for As derived from agricultural use to occur. Streambed sediments would likely contain materials originating from this layer since it is exposed and most subject to erosion. Land use categories may also contain samples with anomalous As concentrations that do not represent those found in the majority of soils from these areas. This is supported by median As concentrations that are significantly lower than the mean As concentrations. Furthermore, land use classification methods did not account for past land use or transfer of material between areas of different land use. Each of these factors creates difficulties in identifying As sources to the soils and sediments collected.

The median As concentrations in the soils and sediments collected from forested areas (7.2 μg/g) corresponds well with the mean As concentration reported for uncontaminated US soils of 7 μg/g although it is higher than the reported world mean As concentration of 5 μg/g in soils. A total of 42.9% of all soil samples exceed the CCME EQG for As in soils of 12 μg/g and 7.1% of all beach sands exceed the CCME EQG marine ISQG for As of 7.2 μg/g. However, arsenic toxicity is highly dependent on speciation and concentrations reported here are for total arsenic. Additionally, the digestion method used in this research allows dissolution of compounds that would not be bioavailable under typical conditions.

Appendix A: Site and sample descriptions and details

Sample ID	Date	Time (HST)	Latitude	Longitude	Site Description	Land Use[b]	Notes	Munsell Color (dry)	Type[a]	Sample Description
001	24-Jul-06	15:05:00	N 21.37299	W 157.76292	Maunawili Valley Park, Olomana	F	Sample taken from dirt patch between pavillon and baseball field at 15 cm depth.	5YR 4.5/6	S	red soil, patches of black clay, low moisture
002	25-Jul-06	6:25:00	N 21.30759	W 157.79858	Wa'ahila Ridge State Recreation Area	F	Sample taken under norfolk pines near pavillon at 15 cm depth.	5YR 3.5/4	S	dark red soil, low to moderate moisture
003	25-Jul-06	7:46:00	N 21.30497	W 157.65544	Makapu'u Lighthouse Trailhead	M	Sample taken from black clay pit (filled now) next to new parking lot at 15-20 cm depth. Evaporites (desert rose) present.	10YR 5.5/1	S	black clay-like soil, very compact, very low moisture
004	25-Jul-06	8:54:00	N 21.40058	W 157.76529	Kapa'a Quarry Road, Kawanui Marsh	M	Sample taken from edge of marsh nearest model airplane field parking lot at 10-15 cm depth.	7.5YR 4.5/6	S	red soil, fine grain, moderate moisture
005	25-Jul-06	9:43:00	N 21.38404	W 157.80458	Ho'omaluhia Botanical Gardens, Kahua Lehua section	A	Sample taken from grassy area mauka parking lot at 15-20 cm depth.	10YR 4.5/4	S	red soil, patches of yellow clay, moderate to high moisture
006	29-Jul-06	10:53:00	N 21.57355	W 158.23024	Mokuleia climb spot	F	Sample taken below 'Beat da Burn' route at 20-25 cm depth.	7.5YR 4/3	S	red soil, low moisture

Appendix A (continued): Site and sample descriptions and details

Sample ID	Date	Time (HST)	Latitude	Longitude	Site Description	Land Use[b]	Notes	Munsell Color (dry)	Type[a]	Sample Description
007	31-Jul-06	12:48:00	N 21.31221	W 157.78024	Ka'au Crater Trail, Palolo Valley, Honolulu Watershed Forest Preserve	F	Sample taken in forest just off trail ~ 10 m before first crossing of Waiomao Stream at 15-20 cm depth. Detritus layer ~ 2 cm removed.	7.5YR 3.5/4	S	dark red soil, moderate moisture
008	02-Sep-06	9:02:00	N 21.28075	W 157.68264	Koko Crater Trail	F	Sample taken just before steep ascent over natural arch at 10-15 cm depth.	10YR 5/1	S	soil with lithofied grey-black ash and white coral fragments, low moisture
009	02-Sep-06	10:17:00	N 21.28303	W 157.68264	Koko Crater Trail	F	Sample taken from wind protected area just below crater rim at 7-10 cm depth.	10YR 4.5/6	S	red-brown soil, very compact, low moisture
010	02-Sep-06	11:47:00	N 21.28606	W 157.68219	Koko Crater Botanical Gardens, Hawaiian section	A	Sample taken near loulu palm grove at 10-15 cm depth. Detritus cover ~ 2 cm removed prior to sampling.	10YR 3.5/4	S	red soil, low moisture
011	02-Sep-06	16:10:00	N 21.35583	W 157.90500	Salt Lake	M	Sample taken from marsh area surrounding the lake at 25 cm depth. Access thru Salt Lake District Park fence. Completely saturated with noticeable H_2S odor.	5YR 3.5/4	S	dark black-brown soil, fine grain sediments

Appendix A (continued): Site and sample descriptions and details

Sample ID	Date	Time (HST)	Latitude	Longitude	Site Description	Land Use[b]	Notes	Munsell Color (dry)	Type[a]	Sample Description
012	03-Sep-06	9:14:00	N 21.26266	W 157.81865	Kapi'olani Park, Waikiki	U	Sample taken under banyan tree across from the tenis courts at 10 cm depth. Detritus layer ~ 5 cm thick.	10YR 3.5/2	S	dark black soil, organic rich, moderate moisture
013	03-Sep-06	11:30:00	N 21.35252	W 157.86002	Kupehau Park, Kalihi Valley	U	Sample taken just off paved path near Kalihi Stream at 10 cm depth. Grass cover removed prior to sampling.	10YR 4.5/3	S	dark soil, compact, moderate moisture
014	03-Sep-06	12:20:00	N 21.38511	W 157.95354	Neal Blaisdell Park, Waimalu	M	Sample taken from adjacent field ~ 2 m from Waimalu Stream at 15 cm depth.	5YR 3/4	S	red soil to 12cm depth; gray-brown sediments with considerably more clay below, compact
015	03-Sep-06	13:06:00	N 21.39709	W 157.90555	Keaiwa Heiau State Recreation Area, Aiea Heights	F	Sample taken from wooded area at 12 cm depth. Leaf debris cleared proir to sampling.	2.5YR 3.5/4	S	Red soil, high moisture, numerous rocks
016	03-Sep-06	14:14:00	N 21.42986	W 157.93669	Manana Trail, Pacific Palisades	F	Sample taken from exposed soil outcrop < 0.4 km from trailhead.	10YR 5/4	S	mix of black and red soil, high moisture

Appendix A (continued): Site and sample descriptions and details

Sample ID	Date	Time (HST)	Latitude	Longitude	Site Description	Land Use[b]	Notes	Munsell Color (dry)	Type[a]	Sample Description
017	04-Sep-06	10:35:00	N 21.36907	W 157.99483	Waipio Soccer Complex	M	Sample taken on Middle Loch side of the pennisula at 12 cm depth.	7.5YR 3/3	S	red soil, low moisture
018	04-Sep-06	11:20:00	N 21.39087	W 158.02765	Hoaeae Community Park, Village Park	U	Sample taken from exposed dirt outcrop on mauka side at 12 cm depth.	5YR 4/4	S	red soil, low moisture
019	04-Sep-06	12:46:00	N 21.54918	W 158.24127	Kaena Point State Park, Yokohama Bay	F	Sample taken mauka parking lot from haole koa grove at 15 cm depth. Area was burnt recently; black ash layer that was removed before sampling.	10YR 3.5/2	S	dark brown soil, low moisture
020	04-Sep-06	13:19:00	N 21.47500	W 158.19443	Makaha Valley Country Club	M	Sample taken from exposed dirt outcrop on SW side of parking lot at 12 cm depth.	5YR 3.5/4	S	red soil, low moisture
021	04-Sep-06	13:43:00	N 21.44819	W 158.18658	Waianae Pilia'au Field	U	Sample taken behind skate park under tree 10-12 cm depth.	2.5Y 4/2	S	dark brown soil
022	04-Sep-06	14:14:00	N 21.45802	W 158.16420	Kaupuni Neighboorhood Park, Waianae Homesteads	U	Sample taken from mauka side at 12 cm depth.	5YR 4.5/6	S	brown-red soil

Appendix A (continued): Site and sample descriptions and details

Sample ID	Date	Time (HST)	Latitude	Longitude	Site Description	Land Use[b]	Notes	Munsell Color (dry)	Type[a]	Sample Description
023	04-Sep-06	14:51:00	N 21.36438	W 158.08635	Makakilo Community Park	U	Sample taken behind baseball field at 15 cm depth.	7.5YR 4.5/3	S	dark brown soil
024	04-Sep-06	15:23:00	N 21.33503	W 158.07785	Kapolei Regional Park	U	Sample taken under St. John's orchid trees at 10 cm depth.	5YR 3/4	S	red soil
025	05-Sep-06	11:47:00	N 21.41689	W 158.00728	Central Oahu Regional Park, Waikele	M	Sample taken from floodplain in middle of park at 10 cm depth.	2.5YR 3.5/6	S	red-brown soil, high moisture
026	05-Sep-06	12:36:00	N 21.44245	W 158.01855	Mililani District Park	U	Sample taken from exposure along north wall at 10 cm depth.	5YR 3.5/4	S	red soil, low moisture
027	05-Sep-06	13:08:00	N 21.45766	W 158.00383	Kipapa Community Park, Mililani Town	U	Sample taken under monkeypod tree near roadside tables at 10 cm depth.	5YR 3.5/4	S	red soil, low moisture
028	05-Sep-06	14:13:00	N 21.49164	W 158.02559	Wahiawa Freshwater State Park	U	Sample taken at unmarked trailhead across easment from transformer in exposed dirt at 10-12 cm depth.	7.5YR 3/4	S	brown soil, low moisture
029	05-Sep-06	15:01:00	N 21.55531	W 158.06100	Pineapple fields, Kamehameha Highway 99	A	Sample taken from exposed soil outcrop along the west side of road at 10 cm depth.	5YR 3/4	S	red-brown soil, low moisture

Appendix A (continued): Site and sample descriptions and details

Sample ID	Date	Time (HST)	Latitude	Longitude	Site Description	Land Use[b]	Notes	Munsell Color (dry)	Type[a]	Sample Description
030	05-Sep-06	15:41:00	N 21.55517	W 158.06096	Pineapple fields, Kamehameha Highway 99	A	Sample taken in fields at 15-17 cm depth.	5YR 3/4	S	dark brown soil, low moisture
031	05-Sep-06	16:14:00	N 21.64068	W 158.06233	Waimea Beach	B	Sample taken near river bank at 12-15 cm depth.	2.5Y 8/2	B	golden sand
032	05-Sep-06	17:10:00	N 21.64210	W 158.02496	Pupukea Paulmalu Forest Preserve	F	Sample taken to right of gate to Kaunala Trail near the Boy Scout Camp at 10 cm depth.	5YR 4/3.5	S	dark brown soil with rocks
033	05-Sep-06	18:24:00	N 21.60858	W 157.91577	Hau'ula Forest Preserve	F	Sample taken from right side of the trail ~ 90 m mauka the Hau'ula Loop trailhead at 10 cm depth.	10YR 5/4	S	dark brown soil
034	05-Sep-06	18:52:00	N 21.55638	W 157.87547	Kahana Bay Beach	B	Sample taken in picinic area at 12 cm depth.	10YR 7/2	B	brown sandy soil
035	14-Apr-07	11:55:00	N 21.32160	W 157.76909	Mau'umae Trail, Mau'umae Ridge, Honolulu Watershed Preserve	F	Sample taken on grassy knoll in view of Ka'au Crater and waterfall under large tree overhanging trail before ohia grove at 12-17 cm depth. Plant debris removed before sampling. (Lanipo hike, map point E)[c]	10YR 4/2	S	dark brown-black soil, high moisture, few rocks, fine roots

Appendix A (continued): Site and sample descriptions and details

Sample ID	Date	Time (HST)	Latitude	Longitude	Site Description	Land Use[b]	Notes	Munsell Color (dry)	Type[a]	Sample Description
036	14-Apr-07	12:20:00	N 21.31669	W 157.77101	Mau'umae Trail, Mau'umae Ridge, Honolulu Watershed Preserve	F	Sample taken in ironwood stand just off trail at 5-10 cm depth. Debris layer ~ 5 cm cleared prior to sampling. (Lanipo hike, between map points D and E)[c]	10YR 4/3	S	light brown-red soil, heavily rooted, low moisture
037	14-Apr-07	12:43:00	N 21.31311	W 157.77307	Mau'umae Trail, Mau'umae Ridge, Honolulu Watershed Preserve	F	Sample taken just off trail at 10-15 cm depth. (Lanipo hike, between map points C and D)[c]	7.5YR 3.5/3	S	red-brown soil, fluffy, low moisture, few rocks, large bark and wood chips, fine roots
038	14-Apr-07	13:07:00	N 21.30921	W 157.77667	Mau'umae Trail, Mau'umae Ridge, Honolulu Watershed Preserve	F	Sample taken next to small ohia after ironwood stand at 7-12 cm depth. (Lanipo hike, map point D)[c]	10YR 5/3	S	brown-red soil with a variety of colored components (black, white, bright red, yellow), compact, highly granulated, low to moderate moisture
039	05-May-07	11:56:00	N 21.64484	W 158.01305	Kaunala Trail, Pupukea Paumalu Forest Preserve	F	Sample taken beside fern covered knoll in paperbark stand at 7-10 cm depth. (Kaunala hike, map point E)[c]	7.5YR 4/4	S	dark red-brown soil, clay-like, moderate moisture, compact, roots

Appendix A (continued): Site and sample descriptions and details

Sample ID	Date	Time (HST)	Latitude	Longitude	Site Description	Land Use[b]	Notes	Munsell Color (dry)	Type[a]	Sample Description
040	05-May-07	12:28:00	N 21.64690	W 158.00693	Kaunala Trail, Pupukea Paumalu Forest Preserve	F	Sample taken on windward side of dirt road leading to Paumalu Girlscout Camp at 5-10 cm depth.	7.5YR 5/4	S	brown soil, compact, low to moderate temperature
041	06-May-07	12:24:00	N 21.53538	W 157.89204	Nakoa Trail, Kahana Valley	F	Sample taken just before hala tree clearing and bunkers at the "4 corners" at 12 cm depth.	10YR 5/4	S	dark brown soil with red and light brown spotting, high moisture, fine roots
042	06-May-07	13:35:00	N 21.52879	W 157.89829	Nakoa Trail, Kahana Valley	F	Sample taken at stream crossing at the farthest extent of the second loop at 12 cm depth.	10YR 4.5/3	S	dark brown soil, high moisture
043	19-May-07	10:04:00	N 21.28796	W 157.84642	Ala Moana Beach Park	B	Sample taken from surface on beach near Magic Island between first and second lifeguard towers ~ 15-20 m from ocean.	2.5Y 8/1	B	white sand, small to medium grain size, larger coral fragments
044	19-May-07	10:56:00	N 21.27400	W 157.82434	Kuhio Beach, Waikiki	B	Sample taken from surface on beach in front of lagoon ~ 10 m from ocean.	2.5Y 8/1	B	white sand, small to medium grain size, larger coral fragments

Appendix A (continued): Site and sample descriptions and details

Sample ID	Date	Time (HST)	Latitude	Longitude	Site Description	Land Use[b]	Notes	Munsell Color (dry)	Type[a]	Sample Description
045	23-May-07	9:23:00	N 21.28569	W 157.67137	Sandy Beach Park	B	Sample taken from surface on beach near east lifeguard tower ~ 3-4 m from ocean.	2.5Y 8/2	B	golden sand, medium grain
046	23-May-07	9:43:00	N 21.33154	W 157.69286	Waimanalo Beach Park	B	Sample taken from surface on beach ~ 60 m south of lifeguard tower and ~ 3 m from the ocean.	10YR 8/2	B	white sand, fine to small grain, larger coral fragments
047	23-May-07	13:39:00	N 21.32942	W 157.89864	Ke'ehi Lagoon Beach Park	B	Sample taken from surface on beach by canoes ~ 1-2 m from ocean.	10YR 8/1.5	B	golden sand, medium to coarse grain, larger fragments
048	23-May-07	14:10:00	N 21.30108	W 157.87703	Sand Island State Park	B	Sample taken from surface on beach at Honolulu side ~ 3-4 m from ocean.	2.5Y 8/2	B	golden sand, corase grained, larger fragments
049	24-May-07	13:03:00	N 21.54911	W 158.24236	Ka'ena Point State Park, Yokohama Bay	B	Sample taken from surface on beach ~ 3-4 m from ocean.	2.5Y 8/1	B	golden sand, medium to coarse grain, few larger fragments
050	24-May-07	13:57:00	N 21.42316	W 158.17908	Maili Beach Park	B	Sample taken ~ 30 m south of lifeguard tower and ~ 15 m from ocean.	10YR 8/1.5	B	golden sand, medium to coarse grain, larger fragments

Appendix A (continued): Site and sample descriptions and details

Sample ID	Date	Time (HST)	Latitude	Longitude	Site Description	Land Use[b]	Notes	Munsell Color (dry)	Type[a]	Sample Description
051	24-May-07	14:37:00	N 21.35994	W 158.13197	Kahe "Tracks" Beach Park	B	Sample taken from surface on beach ~ 8-10 m from ocean.	10YR 8/2	B	golden sand, medium grain, larger fragments
052	24-May-07	15:06:00	N 21.33747	W 158.03813	Ewa Mahiko District Park	U	Sample taken beside baseball diamond on Honolulu side at 7 cm depth.	10YR 4.5/3	S	brown soil, low moisture, roots
053	24-May-07	15:35:00	N 21.30513	W 158.03035	One'ula Beach Park, Ewa	B	Sample taken from surface on beach ~ 3 m from ocean.	2.5Y 8/1	B	golden white sand, small-medium grain, few larger fragments
054	27-May-07	7:56:00	N 21.50733	W 157.98804	Kawailoa Forest Preserve, Wahiawa	F	Sample taken on trail at end of California Avenue next to water tower at 7 cm depth.	7.5YR 4/6	S	red soil, moderate to high moisture
055	27-May-07	8:49:00	N 21.58228	W 158.19263	Mokuleia Beach Park	B	Sample taken from surface on beach ~ 3-4 m from the ocean.	10YR 8/1.5	B	golden sand, medium-coarse grain, very few larger fragments
056	27-May-07	9:28:00	N 21.59796	W 158.10349	Haleiwa Beach Park	B	Sample taken from surface on beach in front of Vietnam War Monument ~ 4 m from ocean.	2.5Y 7/3	B	golden sand, medium grain, very few larger fragments

* indicates digestion replicate

[a] B - beach sand, S - soil

[b] A - agriculture, U - urban, F - forested, M - mixed, B - beach sand

[c] refers to *The Hiker's Guide to O'ahu* by Stuart M. Ball Jr.

Appendix B: Digestion information

Digestion #	Date	Bomb #	Bottle ID (digestion# - sampleID)	Sample Weight (g dry)	Sample Weight (g wet)	Notes
1	31-Mar-07	1	D1-001	0.2075	101.5829	
1	31-Mar-07	2	D1-002	0.1968	103.1287	
1	31-Mar-07	3	D1-007a*	0.2122	95.2888	
1	31-Mar-07	4	D1-003	0.1985	100.4227	
1	31-Mar-07	5	D1-004	0.2046	108.8664	vessel membrane ruptured
1	31-Mar-07	6	D1-005	0.1975	97.8407	
1	31-Mar-07	7	D1-006	0.2054	99.2597	
1	31-Mar-07	8	D1-007b*	0.1954	102.7915	
1	31-Mar-07	9	D1-008	0.2014	99.1305	
1	31-Mar-07	10	D1-009	0.1984	94.1464	
1	31-Mar-07	11	D1-MESS	0.0996	99.5232	
1	31-Mar-07	12	D1-blank	XXX	100.546	
2	15-Apr-07	1	D2-010	0.2018	104.5642	
2	15-Apr-07	2	D2-011	0.2023	96.609	
2	15-Apr-07	3	D2-014a*	0.206	103.9589	
2	15-Apr-07	4	D2-012	0.201	100.6697	
2	15-Apr-07	5	D2-013	0.2001	97.6243	
2	15-Apr-07	6	D2-014b*	0.1979	98.4176	
2	15-Apr-07	7	D2-015	0.1957	101.7602	
2	15-Apr-07	8	D2-016	0.1982	105.3663	
2	15-Apr-07	9	D2-017	0.1984	94.4271	
2	15-Apr-07	10	D2-018	0.2006	102.0358	vessel membrane ruptured
2	15-Apr-07	11	D2-MESS	0.101	103.0016	
2	15-Apr-07	12	D2-blank	XXX	103.5536	

Appendix B (continued): Digestion information

Digestion #	Date	Bomb #	Bottle ID (digestion# - sampleID)	Sample Weight (g dry)	Sample Weight (g wet)	Notes
3	15-Apr-07	1	D3-019a*	0.1982	96.6668	
3	15-Apr-07	2	D3-020	0.1953	101.4022	
3	15-Apr-07	3	D3-019b*	0.2084	101.1465	
3	15-Apr-07	4	D3-021	0.1999	99.4228	
3	15-Apr-07	5	D3-022	0.2024	98.8679	
3	15-Apr-07	6	D3-023	0.1969	98.8706	
3	15-Apr-07	7	D3-024	0.1992	102.39	
3	15-Apr-07	8	D3-025	0.1985	101.7425	vessel membrane ruptured
3	15-Apr-07	9	D3-026	0.2038	104.1115	
3	15-Apr-07	10	D3-027	0.2	99.8658	
3	15-Apr-07	11	D3-MESS	0.0998	99.8574	
3	15-Apr-07	12	D3-blank	XXX	104.3171	
4	24-May-07	1	D4-028	0.1973	99.3704	
4	24-May-07	2	D4-029	0.1997	99.4812	
4	24-May-07	3	D4-035a*	0.2047	101.4678	
4	24-May-07	4	D4-030	0.1953	100.7192	
4	24-May-07	5	D4-032	0.1988	99.4262	vessel membrane ruptured
4	24-May-07	6	D4-033	0.1994	100.2832	
4	24-May-07	7	D4-035b*	0.1921	100.5547	incomplete digestion
4	24-May-07	8	D4-036	0.1998	101.4977	
4	24-May-07	9	D4-037	0.1957	102.7199	vessel membrane ruptured
4	24-May-07	10	D4-038	0.1938	101.7076	
4	24-May-07	11	D4-MESS	0.1045	99.0343	
4	24-May-07	12	D4-blank	XXX	102.2504	vessel membrane ruptured

Appendix B (continued): Digestion information

Digestion #	Date	Bomb #	Bottle ID (digestion# - sampleID)	Sample Weight (g dry)	Sample Weight (g wet)	Notes
5	31-May-07	1	D5-031	0.2007	99.2593	
5	31-May-07	2	D5-034	0.1987	see D7	incomplete digestion
5	31-May-07	3	D5-043a*	0.2084	102.8058	
5	31-May-07	4	D5-043b*	0.2028	101.2369	
5	31-May-07	5	D5-044	0.1993	100.1034	vessel membrane ruptured
5	31-May-07	6	D5-045	0.195	100.5129	
5	31-May-07	7	D5-046	0.1964	100.159	
5	31-May-07	8	D5-047	0.1995	101.1693	
5	31-May-07	9	D5-048	0.1986	97.4962	
5	31-May-07	10	D5-049	0.2008	96.496	
5	31-May-07	11	D5-MESS	0.0995	see D7	incomplete digestion
5	31-May-07	12	D5-blank	XXX	100.0295	
6	10-Jun-07	1	D6-039	0.1988	104.0358	vessel membrane ruptured
6	10-Jun-07	2	D6-040a*	0.1992	98.1893	
6	10-Jun-07	3	D6-040b*	0.2058	101.3481	
6	10-Jun-07	4	D6-041	0.2012	101.1691	
6	10-Jun-07	5	D6-042	0.1979	102.4392	
6	10-Jun-07	6	D6-018	0.2009	100.8222	re-do
6	10-Jun-07	7	D6-025	0.2002	99.5266	re-do
6	10-Jun-07	8	D6-032	0.1999	101.7606	re-do; vessel membrane ruptured
6	10-Jun-07	9	D6-035	0.1959	106.1066	re-do; vessel membrane ruptured
6	10-Jun-07	10	D6-037	0.1963	102.1966	re-do
6	10-Jun-07	11	D6-MESS	0.0994	99.541	
6	10-Jun-07	12	D6-blank	XXX	100.9007	

Appendix B (continued): Digestion information

Digestion #	Date	Bomb #	Bottle ID (digestion# - sampleID)	Sample Weight (g dry)	Sample Weight (g wet)	Notes
7	12-Jun-07	1	D7-050	0.1913	103.3179	
7	12-Jun-07	2	D5-034	see D5	100.6913	digestion continued (see digestion 5)
7	12-Jun-07	3	D7-051a*	0.2077	106.3707	
7	12-Jun-07	4	D7-053	0.1985	103.8906	
7	12-Jun-07	5	D7-055	0.1984	100.8182	
7	12-Jun-07	6	D7-056	0.1967	100.2241	
7	12-Jun-07	7	D7-blank	XXX	103.632	
7	12-Jun-07	8	D7-044	0.1975	99.4513	re-do
7	12-Jun-07	9	D5-051b*	0.1971	97.5216	
7	12-Jun-07	10	D7-MESS	0.0985	105.442	vessel membrane ruptured
7	12-Jun-07	11	D5-MESS	see D5	103.191	digestion continued (see digestion 5)
8	05-Jul-07	1	D8-052	0.1999	100.1161	
8	05-Jul-07	2	D8-054	0.2004	97.813	
8	05-Jul-07	3	D8-032a*	0.2078	97.5195	second re-do
8	05-Jul-07	4	D8-032b*	0.2009	101.7663	second re-do
8	05-Jul-07	5	D8-035	0.1981	99.6331	second re-do
8	05-Jul-07	6	D8-039	0.1977	96.8935	re-do; vessel membrane ruptured
8	05-Jul-07	7	D8-MESS	0.101	100.2135	
8	05-Jul-07	8	D8-blank	XXX	79.1112	vessel membrane ruptured

* indicates digestion replicate

REFERENCES

Abernathy, CO; Beringer, M; Calderon, RL; McMahon, T; Winchester, E. 2003. An update on some arsenic programs at the US EPA. In: Chappell, WR; Abernathy, CO; Calderon, RL; Thomas, DJ (editors) Arsenic Exposure and Health Effects V: Elsevier BV, Oxford.

Abernathy, CO; Thomas, DJ; Calderon, RL. 2003. Health effects and risk assessment of arsenic. *J. Nutr.* 133:1536S-1538S.

Appelo, CAJ; Van der Weiden, MJJ; Tournassat, C. Charlet, L. 2002. Surface complexion of ferrous iron and carbonate on ferrhydrite and the mobilization of arsenic. *Environ. Sci. Technol.* 36: 3096-3103.

Bauer, M; Blodau, C. 2006. Mobilization of arsenic by dissolved organic matter from iron oxides, soils and sediments. *Sci. Total Environ.* 354: 179-190.

Bissen, M; Frimmel, FH. 2003. Arsenic – a review: part 1. occurrences, toxicity, speciation, mobility. *Acta Hydrochim. Hydrobiol.* 31: 9-18.

CCME (Canadian Council of Ministers of the Environment). 2002. Summary of existing Canadian environmental quality guidelines. http://www.ccme.ca/assets/pdf/e1_062.pdf

CRC (Chemical Rubber Company). 2007. **CRC Handbook of Chemistry and Physics, 88th Ed.**

De Carlo, EH; Spencer, KJ. 1995. Records of lead and other heavy metal inputs to sediments of the Ala Wai Canal, O'ahu, Hawai'i. *Pacific Science* 49: 471-491.

De Carlo, EH; Dollar, SJ. 1997. Assessment of Suspended Solids and Particulate Nutrient Loading to Surface Runoff and the Coastal Ocean in the Honokowai Drainage Basin, Lahaina District, Maui. Final report to NOAA/Algal Blooms Project and Hawaii State DOH.

De Carlo, EH; Spencer, KJ. 2002. Spatial and temporal variability of trace element cocnetrations in an urban subtropical watershed, Honolulu, Hawai'i. *Appl. Geochem.* 17: 475-492.

De Carlo, EH; Beltran, VL; Tomlinson, MS. 2004. Composition of water and suspended sediment in streams of urbanized subtropical watersheds in Hawai'i. *Appl. Geochem.* 19: 1011-1037.

De Carlo, EH; Tomlinson, MS; Anthony, SS. 2005. Trace elements in streambed sediments of small subtropical streams on O'ahu, Hawai'i: Results from the USGS NAWQA program. *Appl. Geochem.* 20: 2157-2188.

Dubey, B; Townsend, T. 2004. Arsenic and lead leaching from the waste derived fertilizer Ironite. *Environ. Sci. Technol.* 38: 5400-5404.

Frey, FA; Garcia, MO; Roden, MF. 1994. Geochemical characteristics of Ko'olau Volcano: implications of intershield differences among Hawaiian volcanoes. *Geochim. Cosmochim. Acta* 58: 1441-1462.

Feinglass, EJ. 1973. Arsenic intoxication from well water in the United States. *N. Engl. J. Med.* 288: 828-30.

Fulton, W; Pendall, R; Nguyen, M; Harrison, A. 2001. Who sprawls the most? How growth patterns differ across the US. *Brookings Institution, Center on Urban and Metropolitan Policy,* Survey Series, Washington, DC.

Giambelluca, TW; Lau, LS; Fok, YS; Schroeder, TA. 1984. Rainfall frequency study for O'ahu: State of Hawai'i. *Department of Land and Natural Resources, Division of Water and Land Development*, Report R-73.

Goldschmidt, VM. 1958. **Geochemistry**, Muir, A, editor: Oxford University Press, Oxford.

Hill, BR; Fuller, CC; De Carlo, EH. 1997. Fluvial transport of atmospherically deposited quartz and ^{137}Cs, North Halawa Valley, O'ahu, Hawai'i. *Geomorphology* 20: 67-79.

IUPAC (International Union of Pure and Applied Chemistry). 1997. **IUPAC Compendium of Chemical Terminology, 2nd Ed.** http://www.iupac.org/goldbook/L03540.pdf

Kabata-Pendias, A. 2001. **Trace Elements in Soils and Plants, 3rd Ed.**: CRC Press, Boca Raton.

Li, Y-H. 2000. **A Compendium of Geochemistry: From Solar Nebula to the Human Brain**: Princeton University Press, Princeton, NJ.

MacDonald, GA; Abbott, AT; Peterson, FL. 1983. **Volcanoes in the Sea, 2nd Ed.**: University of Hawai'i Press, Honolulu, HI.

Masscheleyn, PH; Delaune, RD; Patrick, WH. 1991. Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. *Environ. Sci. Technol.* 25: 1414-1419.

Matschullat, J. 1996. Heavy metal contamination of soils: reuse versus disposal. In: Reuther R (editor) **Geochemical approaches to environmental engineering of metals**: Springer, Berlin.

Matschullat, J. 2000. Arsenic in the geosphere – a review. *Sci. Total Environ.* 249: 297-312.

Matschullat, J; Borba, RP; Deschamps, E; Figueiredo, BR; Gabrio, T; Schwenk, M. 2000. Human and environmental contamination in the Iron Quadrangle, Brazil. *Appl. Geochem.* 15: 181-190.

Mizuta, N; Mizuta, M; Ito, F et al. 1956. An outbreak of acute arsenic poisoning caused by arsenic contaminated soy sauce. *Bull. Yamaguchi Med. Sch*. 4: 131.

Montaser, A. 1998. **Inductively Coupled Plasma Mass Spectrometry**: Wiley-VCH, New York.

NRC (National Research Council). 1999. **Arsenic in Drinking Water**: National Academy Press, Washington DC.

Onishi, H. 1969. Arsenic. In: Wedepohl, KH (editor) **Handbook of Geochemistry**: Springer, Berlin.

Pais, I., and Jones, Jr., J.B. 1997. **The Handbook of Trace Elements**: St. Lucie Press, Boca Raton, FL.

Patterson, S.H. 1971. Investigation of ferruginous bauxite and other mineral resources on Kauai and a reconnaissance of ferruginous bauxite deposits on Maui, Hawaii. U.S. Geological Survey Professional Paper 656, U.S. Government Printing Office, Washington, DC.

Reynolds ES. 1901. An account of the epidemic outbreak of arsenical poisoning occurring in beer drinkers in the north of England. *Lancet* i: 166-70.

Robinson, GR; Ayotte, JD. 2006. The influence of geology and land use on arsenic in stream sediments and ground waters in New England, USA. *Appl. Geochem.* 21: 1482-1497.

Roses, OE; Garcia Fernandez, JC; Villaamil, EC et al. 1991. Mass poisoning by sodium arsenite. *J. Toxicol. Clin. Toxicol.* 29: 209-13.

Sansone, FJ; Benitez-Nelson, CR; Resing, JA; De Carlo, EH; Vink, SM; Heath, JA; Huebert, BJ. 2002. Geochemistry of atmospheric aerosols generated from lava-seawater interactions. *Geophys. Res. Lett.* 29.

Smedley, PL; Kinniburgh, DG. 2002. A review of the source behaviour and distribution of arsenic in natural waters. *Appl. Geochem.* 17: 517-568.

Smith, AH; Lingas, EO; Rahman, M. 2000. Contamination of drinking-water by arsenic in Bangladesh: a public health emergency. *Bulletin of the World Health Organization* 78: 1093-1103.

Smith, E; Naidu, R; Altson, AM. 2002. Chemistry of inorganic arsenic in soils: II. effect of phosphorus, sodium, and calcium on arsenic sorption. *J. Environ. Qual.* 31: 557-563.

Spencer, KJ; De Carlo, EH; McMurtry, GM. 1995. Isotopic clues to the sources of natural and anthropogenic lead in sediments and soils from O'ahu, Hawai'i. *Pacific Sci.* 49: 429-510.

Squibb, KS; Fowler, BA. 1983. The toxicity of arsenic and its compounds. In: Fowler, BA (editor) **Biological and Environmental Effects of Arsenic**: Elsevier, New York.

Stearns, H. 1985. **Geology of the State of Hawai'i**: Pacific Books Publishers, Palo Alto.

Stoeppler, M. 1992. Arsenic. In: **Hazardous Metals in the Environment**: Elsevier, New York.

Tamaki, S; Frakenberger Jr., WT. 1992. Environmental biochemistry of arsenic. *Rev. Environ. Contam. Toxicol.* 124: 79-110.

Thomas, R. 2004. **Practical Guide to ICP-MS**: Marcel Dekker Inc., New York.

Vaughan, DJ. 2006. Arsenic. *Elements* 2: 71-75.

Wedepohl, KH. 1995. The composition of the continental crust. *Geochim. Cosmochim. Acta* 59: 217-1232.

Wheat, CG; Jannash, HW; Kastner, M; Plant, JN; De Carlo, EH. 2003. Seawater transport and reaction in the upper oceanic basaltic basement: chemical data from continuous monitoring of sealed boreholes in a ridge flank environment. *Earth and Plant. Sci. Lett.* 6867: 1-16.

Yamashita N; Doi M; Nishio M. 1972. Recent observations of Kyoto children poisoned by arsenic tainted Morinaga dry milk. *Jpn. J. Hygiene* 27: 364-99.